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AN ELECTRON MICROPROBE STUDY OF LUMINESCENCE CENTERS IN CASSITERITE

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ABSTRACT

Using a microprobe equipped with interference filters for making luminescence measurements, the intensity of cathodo-luminescence in zoned cassiterites of hydrothermal origin is found to be directly related to the concentration of the activators Ti and W, provided no quenching combination (Si, Fe), (Fe, W) or (Ta, Nb) is present. Distinct emission bands are observed at ~565 nm for Ti-activation and ~440 nm for W-activation. The Ti-activated emission is similar to the long-wavelength excited fluorescence of the Ca, Sr and Ba metastannates. Iron appears to enhance the Ti-activated emission. An orange cathodo-luminescence is observed when Si is present with Ti in the absence of Fe.

Luminescence intensity exhibits strong thermal quenching, and the activation energy for thermal de-excitation is less than 0.015 eV. The temperature broadening and shift of the peak intensity for the Ti-activated emission are small, and decay time exhibits no appreciable temperature dependence between 21 and 275°C. Thus the Ti-activated emission appears to be a long fluoresence process. The wavelength of W-activated emission is similar to that observed for self-activated $CaWO_4$. The presence of Fe with W suppresses the W-activated emission, while Fe occurring with Ti enhances the probability of luminescence transitions.

Pegmatitic cassiterites that contain Ta and Nb in addition to Fe and Ti, are seldom zoned and exhibit no appreciable cathodo-luminescence, but they are usually pleochoric. It appears that both pleochroism and luminescence-quenching in cassiterites are related to the presence of Ta and Nb.

INTRODUCTION

As early as 1879 Crookes reported that certain minerals emit light when bombarded by energetic electrons. This property, known as cathodo-luminescence, has increased the usefulness of the electron microprobe for mineralogic and petrologic studies. Long (1963) used luminescent properties in the identification of minerals during microprobe analysis, and Long and Agrell (1965) pointed out the variation of luminescent intensity with Mn and Fe in zoned calcite. Smith and Stenstrom (1965) surveyed the potential used of cathodo-luminescence in petrology, with particular reference to quartz, feldspars, apatite, and carbonates (including some fossils). Preliminary reports of the present study of luminescence in cassiterite were made by Ribbe and Hall (1966) and Hall and Ribbe (1969).

The advantages of the microprobe in studying cathodo-luminescent minerals arise from the fact that luminenscence intensity, spectral distribution, and the concentration of two or three impurity "activators" can be recorded simultaneously with a spatial resolution of ~1μ diameter. Since both intensity and wavelength of cathodo-luminescence are often functions of the type and concentration of impurities present in a mineral, the electron microprobe can be used to study details of composition and texture which are unobservable with a petrographic microscope and which are, at best, poorly resolved in X-ray scanning images.

EXPERIMENTAL PROCEDURE

Instrumental Modifications. Part of this study was to determine if an Applied Research Laboratories Model EMX-SM microprobe could be adapted to reliably measure luminescence intensity and spectral dispersion simultaneously with intensities of characteristic X-rays from impurity atoms in minerals. The observed intensities in cathodo-luminescent minerals are typically low, hence a dispersive device of high optical efficiency is required. Kyser and Wittry (1964) used a grating spectrometer attached to the microprobe's light optics which is too inefficient to measure the weak luminescence of most minerals. However, interference filters have an effective transmission 10 to 1000 times greater than grating or prism monochromators with the same passband and are easily adapted to the light optical system of the ARL microprobe. The filters transmit up to 45 percent of the light in a passband of 15 to 20 nm.

The Bausch and Lomb reflecting-type optical objective in the ARL microprobe was modified to facilitate the attachment of a dispersive device and a photomultiplier tube[1] (Hall, 1968). The existing window between the microscope illuminator housing and the vacuum chamber was removed, and the illuminator housing was vacuum sealed and extended so as to contain a movable plane mirror which deflects light into the interference filters. To minimize loss due to absorption, ultraviolet transmitting glass (Spectrosil) was used to pass the light from the modified illuminator housing.

At the monocular of the microscope, the divergence angle of the luminescence from a finely focussed electron beam is only a few degrees; therefore, interference filters can be placed in the focal plane of the monocular without collimation. The photomultiplier used was originally part of the ARL secondary electron detection system. Its output was connected to a recorder for intensity measurements of the luminescence spectrum. An X-Y recorder was used when line-scanning the sample; the luminescence or X-ray signal was connected to the Y channel and the linescanning sweep voltage to the X channel. In this way, consecutive scans were made over exactly the same line on the sample for intensity

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[1] The photomultiplier tube was an RCA 4517 (spectral response curve #115 which peaks at 400 nm).

profiles of both luminescence and X-rays. To minimize losses due to contamination of the specimen surface, luminescence was always scanned first. Spectral dispersion curves were obtained by inserting a series of 10 calibrated, narrow-bandpass intereference filters between the source and detector. The optical transmission and spectral sensitivity of the combined system of mirrors, windows, and photomultiplier were determined by making measurements on four standard electro-luminescent panels, kindly donated by V. L. Beswick of the General Electric Company. The intensity measurements for each of the 10 filters covering the range 400–700 nm were then corrected for filter transmission and the above mentioned effects and were plotted versus the wavelength calibration for the respective filter.

Color transparencies were taken with Anscochrome 500 film using a 35 mm camera attached to the monocular tube. The electron beam was defocussed to $\sim 300\mu$ in diameter. The electron beam current was kept low ($\sim 0.5\ \mu$A) to minimize contamination build-up, because the contaminating film selectively absorbs visible luminescence. Exposure times ranged from five to fifteen minutes.

Sample Preparation. Seventeen samples were analyzed in thin section. Two of these, one showing yellow-green luminescent zones and one showing blue zones, were remounted on ultraviolet transmitting glass for light absorption measurements. Another 23 samples were mounted in bulk, polished, and used for the luminescence photographs and for microanalysis. One of these mounted with a high-temperature cement (Sauereisen) together with a small resistance heater and thermocouple in order to determine the variation of the luminescence emission with sample temperature.

LUMINESCENCE THEORY

For a comprehensive discussion of luminescence theory the reader is referred to the works of Williams (1966) and Curie (1963).

EXPERIMENTAL RESULTS

Forty cassiterites from various localities were analyzed with the electron microprobe. Details of individual analyses and the location and source of the specimens are available on request (or see Hall, 1968). The specimens were categorized on the basis of the observed luminescence effects and the kinds of impurities present in significant amounts)Table 1). Cassiterites of type I are pleochroic, contain appreciable amounts of Ta and Nb in addition to Fe and Ti, are usually unzoned and exhibit no appreciable luminescence. Pleochroism in cassiterites has been associated

TABLE 1. AVERAGE COMPOSITION AND RANGE OF IMPURITY CONCENTRATIONS (ELEMENT WT. %) IN CASSITERITES OF THREE DIFFERENT TYPES

Element	Type I		Type II		Type III	
	Average	Range	Average	Range	Average	Range
Si	0.05	n.d.–0.12	0.07	n.d.–0.30	0.05	n.d.–0.65
Ti	0.08	n.d.–0.23	0.21	n.d.–0.79	.13	n.d.–1.14
Mn	0.04	0.01–0.24	—	n.d.–0.01	0	n.d.–0.02
Fe	0.63	0.02–2.59	0.66	0.02–2.26	0.18	n.d.–1.65
Ta	1.97	0.07–4.48	—	—	—	—
Nb	0.58	0.02–3.31	—	—	—	—
W	<0.01	n.d.–0.14	<0.01	n.d.–0.22	0.21	n.d.–0.84

n.d.: not detected.

with the presence of Ta and Nb by Liebenberg (1945) and others. Most type I cassiterites are from pegmatites (*cf.* Deer *et al.*, 1962) and they are often associated with (and mistaken for) columbite and tantalite.

Cassiterites of type II (Plates Ia,b,c)[1] contain appreciable Fe and Ti, usually no W, no Ta or Nb, and exhibit thin parallel zones with moderate to strong yellow luminescence (see Fig. 1a). Cassiterites of type III (Plates Id,e)[1] differ from type II by containing moderate amounts of W, and exhibit moderate to strong blue luminescent zones (see Fig. 1b). Cassiterites of type II and III are of hydrothermal origin and are frequently twinned on {011}.

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[1] The plates are not reproduced here for reasons of economy. The authors will provide Kodachrome prints or transparencies upon request.

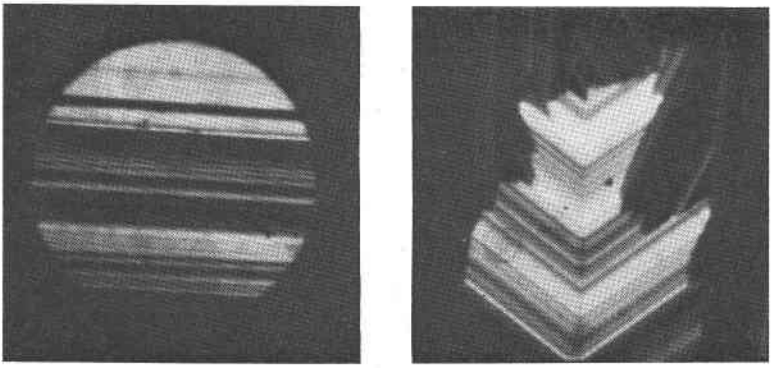

FIG. 1. (a) Yellow luminescent zones in a (Ti, Fe)-activated cassiterite. Circle radius is 220 μ. (b) Blue luminescent zones in a W-activated cassiterite. Barely visible zones in upper center are orange, resulting from (Si, Ti) activators. The photograph is 150 microns square.

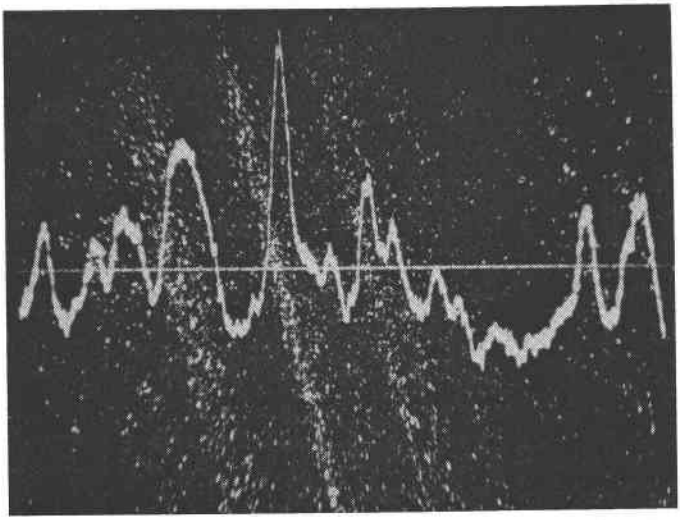

FIG. 2. X-ray scanning image of Fe zoning in cassiterite. The horizontal straight line is the trace of the scan. Iron concentration ranges between none detected and 0.37 wt. % (triple exposure).

X-Ray Scanning Images. The X-ray imaging mode of the ARL microanalyzer is not ideally suited to resolving fine detail at low concentrations, but long exposures permitted resolution of some zoning. Figure 2 shows Fe zoning in a type II cassiterite. A line profile superimposed on this image shows the concentration across the center horizontally varying from none detected to 0.37 wt. % in the bright zone to the left of center.

Luminescence and X-Ray Line Scanning Profiles. The quantitative line scanning profiles of Figure 3 show the variation of luminescence with Ti and Fe concentration for a zoned, type II cassiterite. Consecutive scans were made with filters passing the yellow (570 nm) and blue (450 nm) components of the luminescence spectrum. Line scans were then made for Ti and Fe X-rays and these were calibrated against standards. The Fe concentration profile bears a strong resemblance to the luminescence profile over at least the first two-thirds of the scan. Major peaks in the Ti scan occur very near corresponding peaks in the luminescence scan, although finer zoning is observed in the Ti profile than in either the luminescence or Fe profiles. Linear resolution in the luminescence profiles is necessarily poorer, because the volume of luminescence excitation is considerably larger than that of X-ray excitation. Also, the effects of undetermined amounts of quenching impurities and perhaps some con-

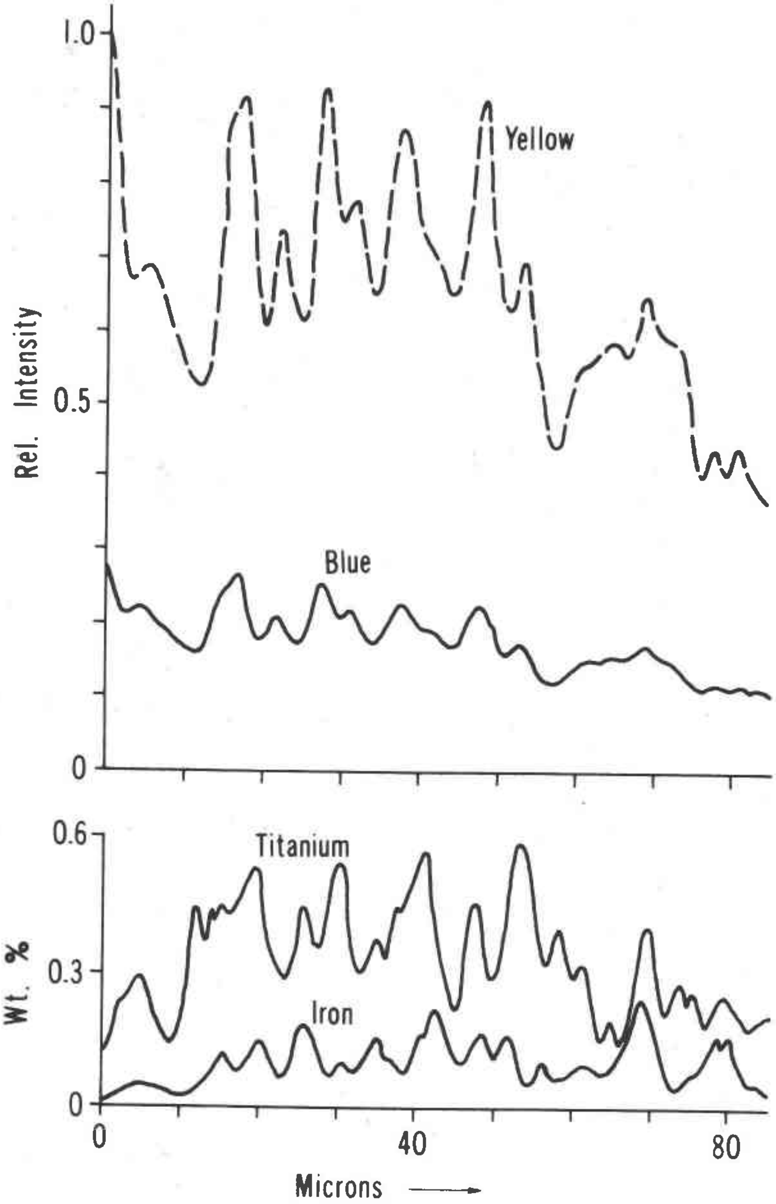

FIG. 3. Luminescence and X-ray line scanning profiles for a zoned cassiterite of type II. Intensities of yellow and blue emissions were corrected for optical transmission and photomultiplier sensitivity using a series of four standard luminescent panels (see text).

centration quenching due to the relatively high levels of Ti and Fe make for inexact comparison between the various profiles. On the whole, however, these profiles support the conclusion that simultaneous increases in both Ti and Fe are associated with increased luminescence.

A similar set of line-scanning profiles for a W-bearing sample of type III is shown in Figure 4. In this scan the similarity between Ti concentration and luminescence intensity is more marked. Note that the amount of Ti is an order of magnitude lower than that for the specimen of Figure 3, so that concentration quenching is less likely. Generally (W+Fe) maxima correlate with minima in the luminescence profiles, while Ti maxima tend to occur with peaks in the luminescence profile. Strong luminescence peaks at 24μ and 49μ in the presence of rather weak Ti maxima but pronounced (W+Fe) minima support the generalization that the combination (W+Fe) acts to quench luminescence. Scans on similar samples support this view; moreover, strong blue luminescence is never observed except in the presence of W which is associated with a distinct emission band centered on about 440 nm (see Fig. 5).

Emission Spectra, Decay Time and the Effect of Temperature. The cathodo-luminescence spectra of Figure 5 exhibits the typical bell-shaped form, which according to Vlam (1954) can be represented as a sum of Gaussian distribution functions when energy is plotted versus wavelength. These indicate an emission band centered at about 565 nm for (Ti,Fe)-activated cassiterite, and two distinct, but incompletely resolved, emission bands for (W,Ti,Fe)-activated cassiterite. The emission band centered near 440 nm is evidently due to the presence of W and is similar to that observed by Leverenz (1946) for self-activated $CaWO_4$. The emission band due to the Ti ion in the W-bearing cassiterite appears to be shifted by ~20 nm to shorter wavelengths.

The decay time for cathodo-luminescence of a type II, (Ti,Fe)-activated cassiterite measured with an oscilloscope (Fig. 6) at ambient temperature is 0.17 m sec. The decay time is not temperature dependent in the range from 21°C to 275°C; therefore, trapping states are apparently unimportant in cassiterite luminescence.

The intensity of the (Ti,Fe)-activated cathodo-luminescence decreases rapidly with increasing specimen temperature (Fig. 7) and appears to be strongly quenched even at room temperature. The (Ti,Fe)-activated emission spectrum at 473°K is shifted (~10 nm) to shorter wavelengths as compared with that at 294°K, and is slightly broadened (~10 nm) at half-maximum intensity.

Absorption and Transmission Measurements. Thin sections of both type

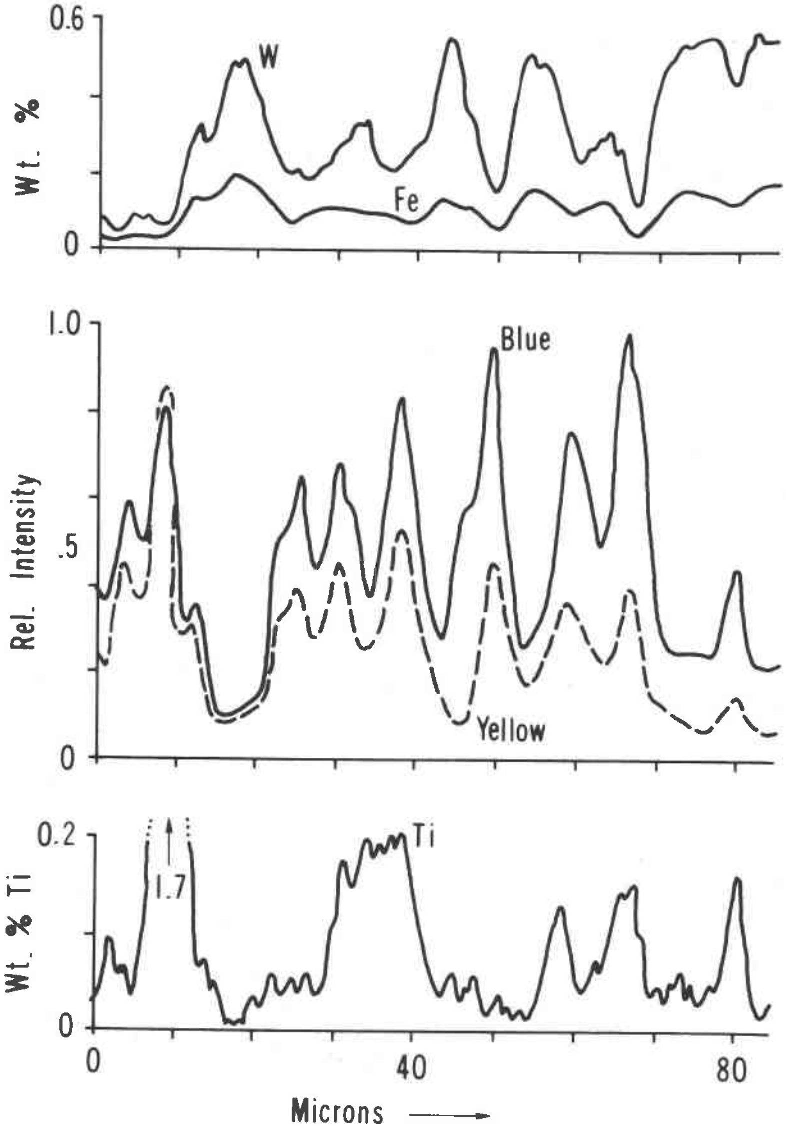

FIG. 4. Luminescence and X-ray line scanning profiles for a zoned cassiterite of type III. Intensities were corrected as described in legend of Fig. 4.

I and type II cassiterite give the same absorption spectra as determined with a monochromatic source. This shows nearly complete absorption over the entire ultraviolet (below 390 nm) range and two absorption

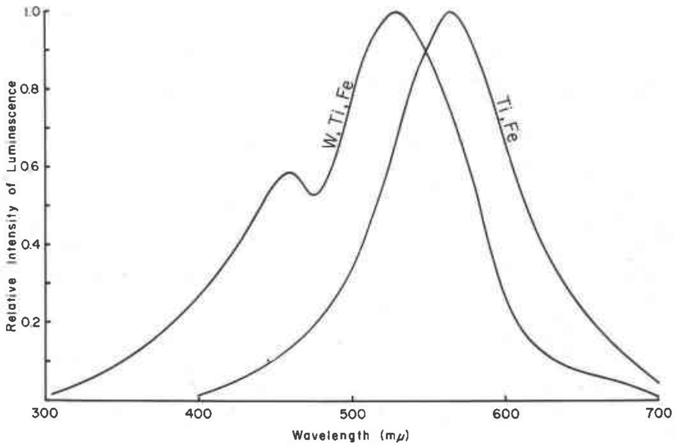

FIG. 5. Typical cathodo-luminescence spectra for (Ti, Fe)-activated and (W, Ti, Fe)-activated cassiterite. Wavelength in nanometers.

peaks near 550 nm and 650 nm (Fig. 8). Transmission measurements made with a polychromatic source show a peak at 565 nm for (Ti,Fe)-activated samples and two peaks at 440 nm and 550 nm for (W,Ti)-activated cassiterite. These correspond identically to the observed cathodoluminescence peaks, and indicate that the samples are weakly photoluminescent.

DISCUSSION

The study of luminescence in natural minerals is limited by the complicated effects of unwanted impurities. A complete description of the luminescence mechanism cannot be based on microprobe studies alone, because analytical sensitivity (~100 ppm) does not extend to levels of purity which may significantly affect luminescence. However, the method can be used to determine the type of activator and to provide some clues to the mechanism.

Titanium-Activated Emission. In cassiterite the X-ray scans correlate Ti and Fe concentration with the yellow luminescence zoning of the type II samples and Ti concentration with the predominately yellow zoning of the type III samples. Thus, Ti is most likely the activator of yellow luminescence, with Fe playing the role of a coactivator or sensitizer in type II samples. Since the luminescence spectra show two distinct emission bands for the samples containing both W and Ti, and since the blue (440 nm) emission occurs only in the presence of W, it would seem that

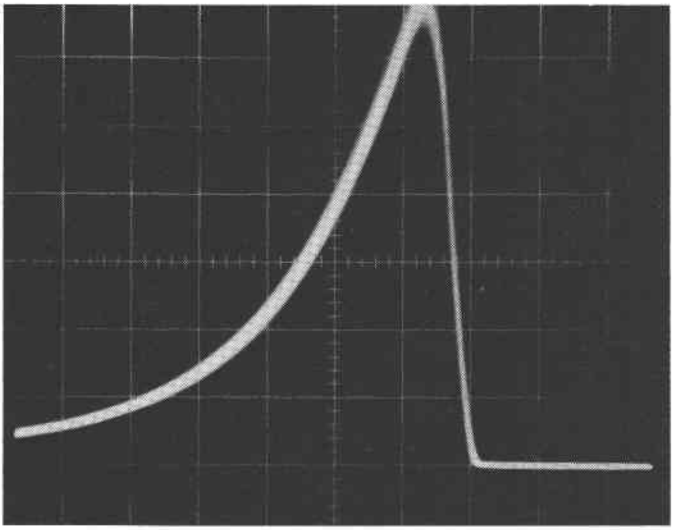

FIG. 6. Decay characteristic for cathodoluminescence of (Ti, Fe)-activated cassiterite as displayed on an oscilloscope. The electron beam was swept rapidly across an isolated, narrow luminescent zone from right to left. The luminescence signal is of negative polarity, so that the falling portion of the trace affords a measure of response time of the measuring system (~0.04 msec.). The luminescence decay time (the difference between rise-time and fall-time of the trace) is 0.17 msec.

W is the impurity activator for the blue emission, although the quenching effect of a (Fe,W) combination complicates the picture.

Kröger (1948) reports that Ti is almost universally effective as an impurity-activator for luminescence, and has observed both long-wave excited yellow-green and short-wave excited blue emissions for Ti-activated metastannates. Ti^{+4} in perovskite structure of these compounds is octahedrally coordinated by oxygen as it is in cassiterite. The Ti-activated luminescence of both the metastannates and cassiterite exhibits strong thermal quenching.

The Role of Fe. The Fe^{2+} and Fe^{3+} ions usually have a quenching effect on visible luminescence (Orgel, 1955) due to infrared transitions which are characteristic of these ions. However, a green emission band for magnesium aluminate spinel under cathode-ray excitation has been reported by Hummel and Sarver (1964) who attribute it to Fe^{3+} tetrahedrally coordinated by oxygen. These workers also observed a deep red band (near 700 nm) which they suggest is probably due to octahedrally coordinated Fe^{3+}. The dark reddish-brown, optically colored zones in cassiterite have been associated with the presence of Fe, primarily Fe^{2+},

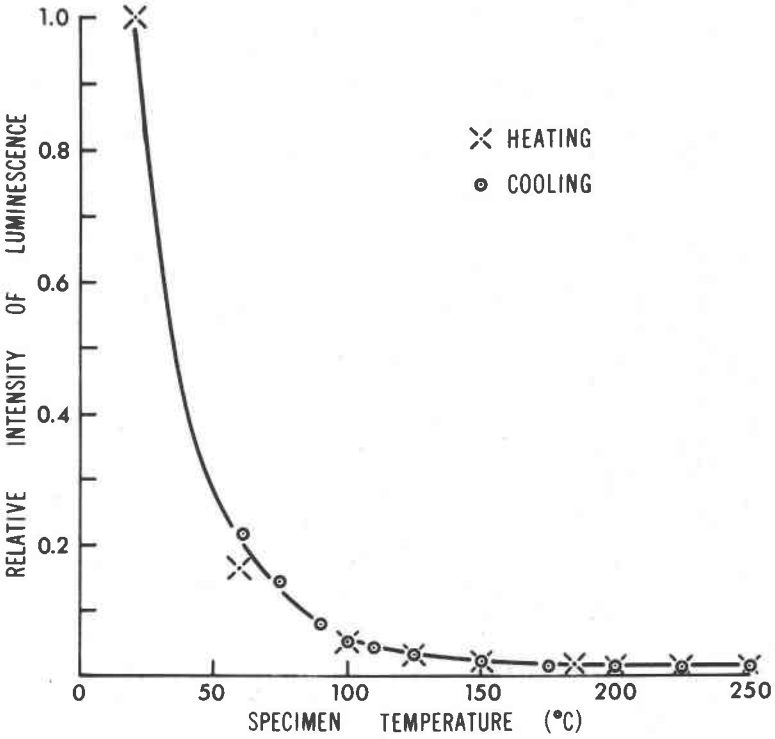

FIG. 7. Temperature dependence of (Ti, Fe)-activated cathodo-luminescence.

in Mössbauer studies of color zoning in cassiterite. Grubb and Hannaford (1966) report that both Fe^{2+} and Fe^{3+} are present in light and dark zones, but Fe^{2+} is more concentrated in the dark zones which are also found to be ferromagnetic.

Tungsten-activated Emission. Leverenz (1946) has also observed blue luminescent bands ($\lambda \sim 485$ nm) in the self-activated monoclinic tungstates $MgWO_4$, $CdWO_4$, and $ZnWO_4$. Randall (1939) had ascribed this emission to the presence of the tungstate ion WO_4^{2-}. The blue emission in cassiterite has nearly the same peak wavelength and spectral dispersion as that reported by Leverenz (1946) for $CaWO_4$ cathodoluminescence, although W is tetrahedrally coordinated in $CaWO_4$ and octahedrally coordinated in cassiterite.

As noted previously, Kröger (1948) found a blue emission band for Ti-activated stannates. Also, Smith (1949) has reported that well-crystallized diopside activated with Ti gives a broad blue emission band

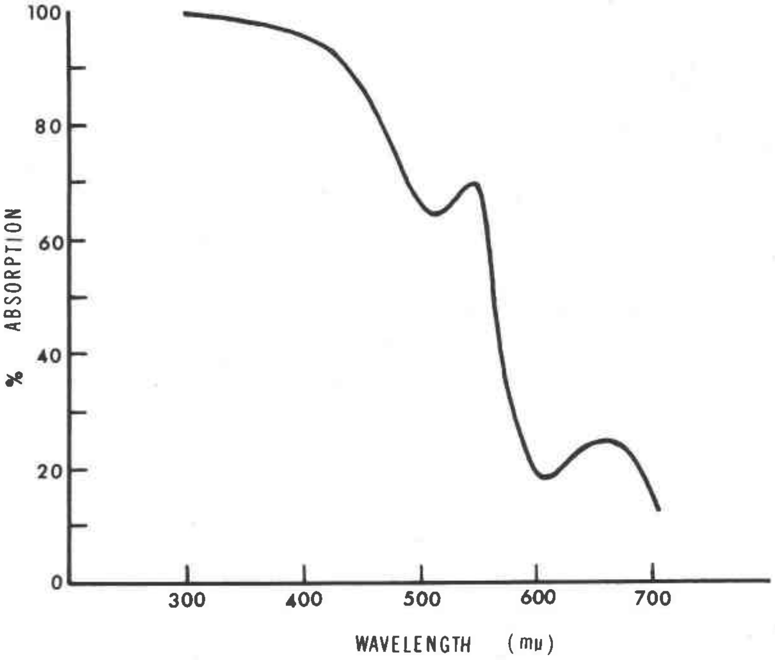

FIG. 8. Absorption spectrum for a type II cassiterite. The strong absorption below 400 nanometers indicates a valence-conduction band gap for SnO_2 of ~3eV. The peaks at 550 nm and 650 nm may correspond to charge-transfer spectra for Ti and Fe.

(λ ~410 nm) under cathode-ray excitation. For cassiterite, however, the blue emission was never observed except in the presence of W. If the oxygenligancy of Ti is responsible for the blue emission, as suggested by Kröger, then we would expect that conditions favoring a blue emission in cassiterite might occur in the absence of W. Lacking such evidence, we interpret the blue emission band for cassiterite to be characteristic of W-activation.

Effect of Ta and Nb. Tantalum and niobium apparently act to quench any luminescence which might otherwise occur. This may account for the fact that Bahezre *et al.* (1961) did not report cathodo-luminescence in a zoned cassiterite which contained Ta, Nb, Fe and Ti. These ions also appear to be responsible for pleochroism in cassiterite. It is possible that Ta and Nb compensate for charge defects introduced by impurities such as Fe or by anion vacancies, but the exact nature of the mechanism is obscured by the effects of other impurities in natural cassiterite and will probably not be fully understood until measurements are made on synthetic crystals with controlled impurity levels.

Emission Band Shifts. Fonda (1957) formulated a "rule" which usually holds for metallic oxide phosphors as well as some sulfides and halides. It relates the shift of spectral emission bands to changes in the cation-anion distances in the compound. The basic reasoning is that the field strength to which the activator center is subjected by its environment of oxygen atoms depends upon the cation-anion bond lengths. Substitution of a larger cation causes structural expansion and a reduction of the fields to which the luminescence center is subjected. As a result, the energy gap between the excited and ground states of the center increases and the luminescence emission band shifts to shorter wavelengths. The rule also holds for structural expansion and contraction due to temperature changes.

The shift (~10 nm) of the emission band for Ti-activated cassiterite to shorter wavelengths is in accord with Fonda's rule; however, the magnitude of the shift indicates that the Ti-center is not strongly disturbed by thermal motion of the oxygen ligands. The high value for the vibrational quantum energy of the excited state, as indicated by the small temperature broadening of the emission bandwidth, also supports this conclusion which is in accord with Kröger's (1948) conclusion that the Ti^{4+} ion plays the major role in determining the optical transitions which give rise to the yellow or yellow-green emission bands.

It is worth noting that the orange luminescence (Plate Ie; *cf.* Fig. 1b) in the presence of Si^{4+} ($r \sim 0.40$ Å) substituting for Sn^{4+} ($r \sim 0.69$ Å) represents a shift of the Ti-activated yellow emission band in accord with Fonda's rule. The shift (~20 nm) of the Ti-activated band in the presence of W^{4+} ($r \sim 0.65$ Å) is not in accord with this rule, although uncertainties about the valence state of W, the small difference in radii, and the effect of trace level impurities present difficulties in explaining this inconsistency. [Ionic radii quoted are from Shannon and Prewitt (1969)].

The strong temperature dependence of the cathodo-luminescence efficiency and negative evidence of thermally active electron traps, as well as the evidence of slight temperature broadening of the bandwidth and small band peak shift, all support the Klasens (1946) model for thermal quenching of luminescence centers. This model attributes thermal quenching to the filling of empty ground states of the luminescence center with electrons thermally excited from the valence band. The activation energy for this model is a measure of the energy difference between the ground state of the center and the top of the valence band, and is estimated to be small (~0.015 eV).

Since the effective ionic radii of octahedrally-coordinated W^{4+} and Sn^{4+} are nearly the same, only small local disturbances of the SnO_2 energy-band structure are to be expected. The three primary excitor elements in cassiterite (Ti,Fe,W) are transition metals. Titanium and Fe ions with partially filled 3d orbitals and W ions with partially filled 5d orbitals can bond with the 2p electrons of the oxygen anions. All three elements produce excited states for luminescence transitions.

Since Ti^{+4} has the electronic configuration of argon, the luminescence mechanism requires charge-transfer in which the metal ion is effectively reduced during excitation (see Orgel, 1966, pp. 103–105). The observed emission and absorption spectra support this deduction which is in accord with Kröger's (1948) observation that the long-wave excited yellow-green emissions from Ti-activated compounds involve transitions localized on the Ti ion.

CONCLUSION

Although the present study has characterized the luminescent properties of cassiterites from more than 20 localities, it is obvious that only a series of experiments in which synthetic cassiterites are carefully doped with luminescence activators and quenchers will produce the kind of detailed information that is now available for ZnS. The chemical complexity of these natural specimens makes it unlikely that the effects of certain impurity combinations will be resolved in any other way.

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