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THERMOLUMINESCENT SPECTRA OF SODIUM CHLORIDE AND HYDROXIDE-FREE SODIUM CHLORIDE IRRADIATED WITH 40-MEV ALPHA PARTICLES

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SUMMARY

The thermoluminescent spectra of 40-Mev alpha-irradiated sodium chloride single crystals have been investigated through postirradiation measurements. Both as-received and hydroxide-free sodium chloride were used. Graphs of the variation of emission band intensity and position as a function of temperature for various radiation fluxes are presented. Emission bands at 360 and 432 millimicrons were found in both crystal types; a new band at 572 millimicrons was also observed in the hydroxide-free crystals. The 432-millimicron band is suppressed in the high-temperature glows of the hydroxide-free crystals. In contrast to X-ray induced spectra the effect of particle irradiation was to cause the 360- and 432-millimicron bands to appear together in the high-temperature glow peaks. Comparison of the glow curves of the two crystal types indicated that the hydroxide-free sodium chloride increased light output. An impurity or defect is thought to be responsible for the effects noted in the hydroxide-free crystals.

INTRODUCTION

Although the effects of radiation on alkali halides have been studied extensively (ref. 1), little has been done on thermoluminescent spectra; the thermoluminescent spectra of heavy-particle-irradiated alkali halides have not been reported. Since the mechanics of radiation damage is not yet fully understood, it was felt that such a study would be useful. In particular, a comparison of the spectra and glow curves of previously published data on X-ray-irradiated sodium chloride (NaCl) (refs. 2 to 4) with the present data may reveal effects due to heavy particle irradiation and give information on the nature of the damage mechanism in each type of irradiation. The spectral analysis of the glow curves from alpha-irradiated NaCl is presented herein. Part of the data is presented in the form of band glow curves. These are curves of the relative emission intensity taken at a fixed wavelength (that of maximum band emission) as a function of temperature.

In the study of radiation effects on NaCl, use of as nearly perfect a crystal as possible is desirable. Recent work on the mechanical properties of NaCl (unpublished data obtained at Lewis) and on the optical properties of NaCl (refs. 5 to 7) has indicated that the presence of sodium hydroxide (NaOH) in synthetic NaCl crystals has a pronounced effect on their properties. The hydroxide is incorporated in the crystals during the growing process. Indication of the presence of hydroxide ions is associated with an optical absorption band at 190 millimicrons in NaCl (ref. 6). Alkalinity measurements also reveal the presence of hydroxide ions (ref. 8). In these measurements the hydroxide was found to be inhomogeneously distributed throughout a given sample. In order to remove the hydroxide some of the crystals were annealed in a hydrogen chloride atmosphere (ref. 9). The results indicate, however, that although the hydroxide is removed an impurity or defect has been added.

EXPERIMENTAL PROCEDURE

Specimens of NaCl were obtained from the Harshaw Chemical Company in the form of 1-inch-diameter cylinders of random lengths. Before annealing, they were cleaved to a thickness of 2 to 3 millimeters. Annealing consisted of heating the specimens in a platinum boat to a temperature of 725° C for 48 hours and then allowing the furnace to cool to room temperature at its natural rate, which took 7 hours. The platinum boat could be inserted into the furnace through a Vycor tube in which the specimens could be exposed to various atmospheres. For the as-received specimens, dry nitrogen gas was used; for the OH-free specimens dry hydrogen chloride gas was used. Both wet chemical (ref. 8) and spectrochemical measurements of the HCl treated crystals revealed no detectable OH concentration, whereas the as-received crystals contained 2 ppm of NaOH.

In order to keep the crystals from shattering due to heating by the alpha beam and to hold bleaching to a minimum, the irradiations were performed at liquid-nitrogen temperature. A metal Dewar with a 1-mil steel foil window was used for the irradiations (fig. 1). The crystals, mounted on appropriate holders, could be positioned very close to the foil face by means of tracks in which the holder traveled so that the alpha beam energy loss in the liquid-nitrogen would be small. To help assure a uniform particle flux, irradiation was done some 20 feet from the 60-inch cyclotron exit port. The beam was adjusted to a 1-inch-diameter spot by means of focus and steering magnets. Since the Dewar also served as a Faraday cup, the total flux was found by integration. Beam currents used varied from 0.01 to 2 microamperes.

The irradiated crystals were stored in the dark at liquid-nitrogen temperature for 20 to 25 hours until the radioactivity decayed. When needed, they were removed from the liquid nitrogen, cleaved, and inserted into the furnace as quickly as possible. Glow peaks below room temperature were allowed to decay before the runs were started. The sample area after cleaving was approximately 1/2 square centimeter so that six to eight samples could be obtained from a single 1-inch-diameter irradiated disk.

The instrumentation used to record simultaneously the glow curves and their components is shown in figure 2. The monochromator, wavelength drive, and lamphouse from a Beckman DK-1 spectrophotometer form the basic unit. The tungsten lamp, which normally acts as the light source, has been replaced by a small furnace. The furnace is positioned so that the crystal specimen when placed in the furnace opening (1 by 1 cm) will be in the same position as the filament of the lamp. A thermocouple placed along the furnace axis contacts the back of the specimen. The light to be analyzed is directed into the monochromator by a mirror while the total light emission is seen by a photomultiplier (RCA 6199) placed opposite the furnace as shown in figure 3. The output of the photomultiplier is fed through a d-c amplifier to a two-pen recorder; the second pen is used to record the temperature. The analyzed light was recorded on a second recorder by using a quartz window photomultiplier (EMI 9552S) and d-c amplifier. To scan the spectrum of interest automatically, a variable speed motor driven cam and switch system was used. Marker pens on each recorder were operated by the cam switch and served to synchronize the system. The scan was calibrated by using a sodium arc lamp. The heating rate of the furnace was linear from 40° to over 300° C and was 0.76° C per second. The monochromator slit openings used were 1 and 2 millimeters. No correction was made for the wavelength response of the photomultipliers. The dark current was balanced out with a bucking voltage introduced at the tube anode.

As an example of the scanning procedure, figure 4 is a presentation of the trace of a recording of an OH-free crystal irradiated to a flux of 10^{12} particles per square centimeter. The scan range is from 330 to 650 millimicrons. Two peaks represent each band because the sweep is oscillating (i.e., upscale, downscale, etc.). Once the band positions were determined, band glow curves (wavelength fixed at maximum band intensity) could be taken.

Absorption spectra of crystals given light to medium irradiations reveal the presence of F, M, and V_3 bands in both types. Only identification of the absorption bands was made. X-ray-irradiated crystals gave similar absorption results. The 572-millimicron emission band is also present in X-ray-irradiated OH-free crystals.

RESULTS

Curves of the relative intensity of the various emission bands as a function of temperature (band glow curves) for various fluxes are shown in figure 5 for as-received NaCl crystals and in figure 6 for OH-free NaCl crystals. In the range scanned (300 to 700 mμ) only three bands were observed, namely, 360, 432, and 572 millimicrons. Representative glow curves and associated band glow curves were selected for each figure (5(a), (b), etc.) by using the criteria of similarity of intensity and peak temperature of the glow curves. Some further adjustments of the data, however, were required, and these are outlined in the appendix.

An examination of figure 5 reveals that as the radiation flux increases, the low-temperature glow peak decreases in intensity relative to the high-temperature peak and finally disappears at the highest flux. Both low- and high-temperature peaks shift to somewhat higher temperatures as the flux is increased - the shift is larger in the low-temperature peak. Two bands, 360 and 432 millimicrons, are found in all peaks - the 360-millimicron band is the dominant one.

Figure 6 indicates that the OH-free crystals follow a pattern similar to the as-received crystals as far as shift of intensity and peak temperatures with flux are concerned; however, the peaks occur at lower temperatures and, generally, have increased intensity. Another band, at 572 millimicrons, is found in all peaks in addition to the 360- and 432-millimicron bands. For the first two flux levels the 432-millimicron band in the high-temperature peaks is suppressed. It is interesting to note that in both crystal types, the band glow peaks are not always coincident. This fact is also evident in figure 4 where the envelope drawn over the instantaneous band peaks shows that the bands do not coincide in the last glow peak; the 572-millimicron band occurs before and in greater intensity than the 360-millimicron band. (Note that the exact band intensity maximums cannot be determined in this fashion.) The 432-millimicron band is not detected in the last peak.

Figure 7 is a comparison plot of typical glow curves (not normalized) of the two crystal types for the three radiation fluxes used. The change in position and intensity of the curves as a function of flux is easily seen, especially the fact that the temperature difference between the peaks of the two crystal types diminishes as a function of increasing flux. Note that in figure 7(b) the as-received glow curve is referred to the right-hand scale. The following table is a presentation of the approximate intensities (arbitrary units) of the average of the high-temperature peaks of the glow curves associated with the emission bands of figures 5 and 6 relative to that of the high-temperature peak of the low flux as-received type.

Flux particles/cm^2	As-received type	OH-free type	Intensity ratio (approx.) (OH free/as received)
2×10^{12}	1	2.4	2.4
10^{14}	2.4	44	18
10^{16}	630	1900	3

The intensities are shown corrected for the fact that they increase with increasing radiation flux. The greatest intensity difference appears in the medium flux range.

DISCUSSION

The thermoluminescent spectra of X-ray-irradiated NaCl has been investigated by several experimenters over the last several years (refs. 2, 3, and 10 to 12). While some reports have merely identified the emission bands (refs. 3 and 10 to 12) and one has recorded individual band peaks (ref. 2), no band glow curves have been reported.

Two of the band wavelengths observed in this experiment (360 and 432 mμ) agree well with the results of others using X-rays (refs. 2 and 3). The 572-millimicron band observed in the OH-free crystals has not been noted, although many bands in the 500- to 600-millimicron region are reported in the literature (refs. 2, 3, and 12). Halperin and Ben-Zvi (ref. 2) reports a band at 510 millimicrons. The present data also demonstrate that two and three different bands can be found in a glow peak. In addition, bands of the same wavelength repeat themselves. This agrees with reference 2 but does not agree with Bonfiglioli, Brovetto, and Cortese (ref. 12), who also analyzed X-ray-irradiated NaCl. They assign a single wavelength to each glow peak.

An examination of the spectra of particle-irradiated NaCl permits investigation of the suggestion of reference 13, that there may be light emission associated with vacancy combinations that take place as the crystal is warmed. The combination of positive and negative ion vacancies to form neutral clusters is postulated from a series of experiments on particle-irradiated crystals reported by Smoluchowski (ref. 14). However, no emission band that could be associated with this process was observed. One of the experiments, that of stored energy measurements, indicates that considerable heat is evolved as an irradiated crystal is warmed at a constant rate. This evolved heat is associated with vacancy and interstitial combinations. Since this is thermal energy, it seems unlikely that these combinations would have high enough energies associated with them to produce visible radiation.

Of present interest is the comparison of the thermoluminescence of alpha-particle-irradiated NaCl with that of X-ray-irradiated NaCl with a view toward identifying, if possible, the effects of atomic displacement by the charged particles. Only results from the as-received crystals are considered here in order to compare, on the same basis, with the work of others. Although the emission bands are similar, the fact that the two bands persist in every glow peak differs from the results obtained from X-ray-irradiated crystals by Halperin and Ben-Zvi (ref. 2). In that reference the two bands (360 and 432 mμ) are listed as being found together in only one X-ray-induced glow peak (62° C).

An examination of the glow curves obtained from X-ray-irradiated crystals (refs. 2 to 4) agrees with the present data in that two glow peaks are present, the low-temperature peak being generally lower in intensity than the high-temperature peak at low and medium doses. At increased dose levels, only the high-temperature peak is present. Glow peak temperatures are also in good agreement. The first glow peak temperature as reported in reference 3 is 87° C, and reference 4 records 67° C. The present data have a range from 62° to 74° C. For light to medium fluxes, the high-temperature glow peaks occur at approximately 240° C, whereas for light and medium X-ray irradiation the last peak is in the range of 200° to 215° C (refs. 2 and 3). At the heaviest irradiations, the positions of the high-temperature peaks are 285° C (ref. 3), 267° C (ref. 4), and 273° C from this investigation. Thus, the glow peak temperatures are a function of total irradiation, regardless of the type of irradiation.

A visual comparison of X-ray-irradiated and particle-irradiated crystals reveals that the color center stability is enhanced in the particle-irradiated crystal. A possible explanation for this is based on an interpretation of color center stability by Varley (ref. 15). He postulates that interstitial halogen atoms, which are ejected from their normal sites by double ionization during irradiation and then rapidly regain one electron, can be trapped at positive ion vacancies. If there are relatively few positive ion vacancies present, as would be the case for X-ray irradiation, it is further postulated that the displaced interstitial halogen atoms will slowly diffuse to negative ion vacancies, thus the number of color centers is reduced by combining with the electrons associated with the vacancies to form chlorine ions. Increasing the positive ion vacancy concentration should then increase color center stability. Divalent doping of NaCl as well as heat treating and crystal growing experiments confirms this (ref. 15). It can also be seen that the relative increase in color center stability of particle-irradiated over X-ray-irradiated crystals may be due to the increase in positive ion vacancies generated by particle displacement, that is, displacement of the sodium ion.

Comparison of the results obtained with OH-free crystals with the as-received crystals reveals an increase in total light emission, shift of the glow peaks to lower temperatures with low and medium irradiations, and a new emission band. The intensity of this new band (572 mμ) decreases with increasing flux. The light from this band does not account for all the increased light emission from the OH-free crystals. In figure 6(b), for example, the 360-millimicron band is the principal contributor. Also the light emission from the OH-free crystals appears to go through a maximum in the medium flux region (see fig. 7).

The preceding results suggest that an impurity or defect may have been introduced into the crystals during the annealing process. Reference 5 demonstrates that F center concentration is proportional to hydroxide concentration and that the introduction of impurities greatly enhances colorability; reference 7 also supports this suggestion by showing that impurity effects are greatest at low and medium irradiations. The nature of the impurity is at present unknown. (Preliminary analysis of OH-free crystals annealed in a Vycor tube without the platinum boat indicate that the impurity is not present since the 572-mμ band is not detected, and the total light output is lower than that from OH-free crystals annealed by using the platinum boat.)

SUMMARY OF RESULTS

The thermoluminescent spectra of 40-Mev alpha-particle-irradiated sodium chloride and hydroxide-free sodium chloride have been investigated. Emission band position and intensity as a function of temperature and radiation flux is presented. Whereas data from X-ray-irradiated crystals indicate two emission bands present in only one glow peak, two bands are observed in every glow peak of the particle-irradiated crystals. For both X-ray and particle irradiation, however, the glow curves exhibit similar changes with increasing irradiation. The hydroxide-free crystals show increased light output as well as a new emission band at 572 millimicrons. The 432-millimicron band is suppressed in the high-temperature glow peaks of the hydroxide-free crystals. The results from the hydroxide-free crystals suggest the introduction of an unknown impurity from the annealing process. An increased color center stability of particle-irradiated crystals over X-ray-irradiated crystals is noted and discussed.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, December 18, 1962

APPENDIX - ADJUSTMENTS TO BAND GLOW CURVES

In order to present the several emission bands in one figure (5(a),(b), etc.) for each flux rather than having individual figures of emission and glow curves, the following adjustment of the data was made. To compensate for amplifier gain factor changes from run to run, the emission intensities were normalized to the maximum amplifier gain. Then the band intensities in each figure were multiplied by their associated normalizing factors found from the glow peaks. That is, the factor used to adjust a glow peak to the maximum glow peak intensity associated with a given figure was used to adjust the emission intensity that goes with that particular glow curve. To correct the emission bands for the fact that the peak total light intensities for a given flux do not always occur at the same temperature, the bands have been shifted in temperature by the same amount needed to make the glow curves coincident about one of the glow curve peaks. The shift was no more than 15° and usually between 2° and 6° C. The following table lists the adjusted glow curve peak temperatures:

Figure	Low-temperature glow peak, °C	Medium-temperature glow peak, °C	High-temperature glow peak, °C
5(a)	74	---	236
5(b)	--	114	243
5(c)	--	---	273
6(a)	62	---	195
6(b)	72	131	226
6(c)	--	---	267

The foregoing adjustments also have the effect of compensating for inhomogeneous radiation flux and size of furnace specimen. No relation between the figures is implied, since correction for increasing light output with increasing flux was not made.

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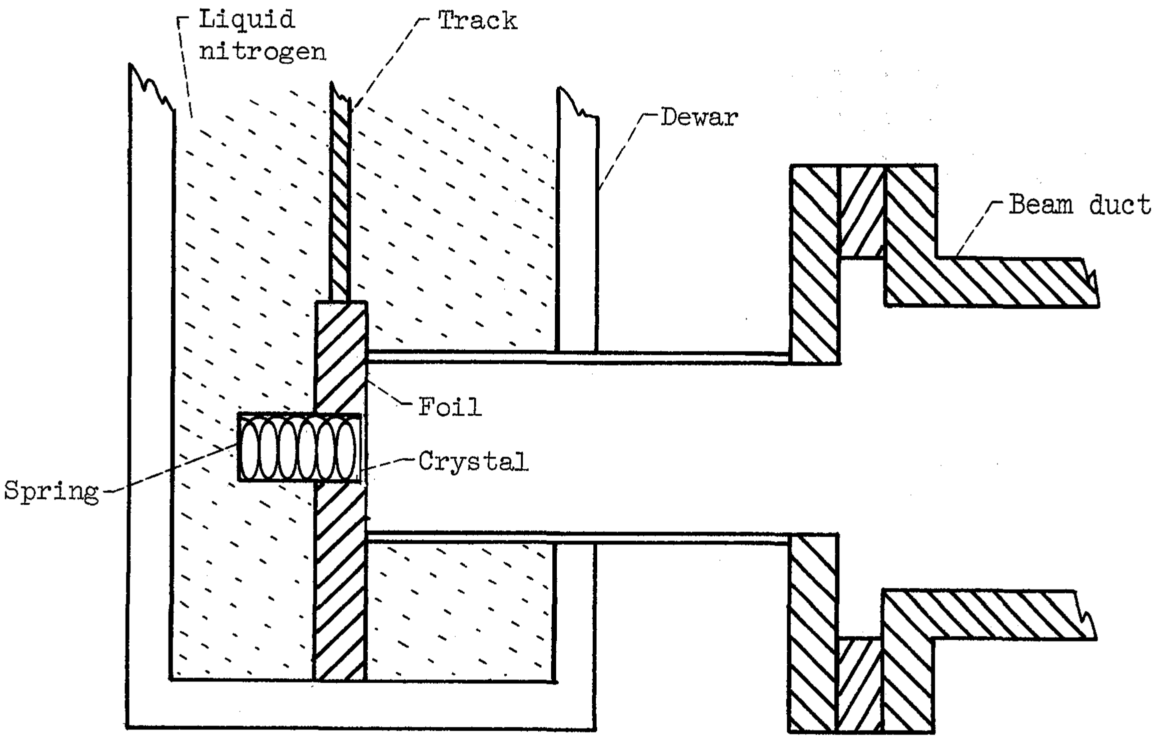


Figure 1. - Dewar in position on beam duct.

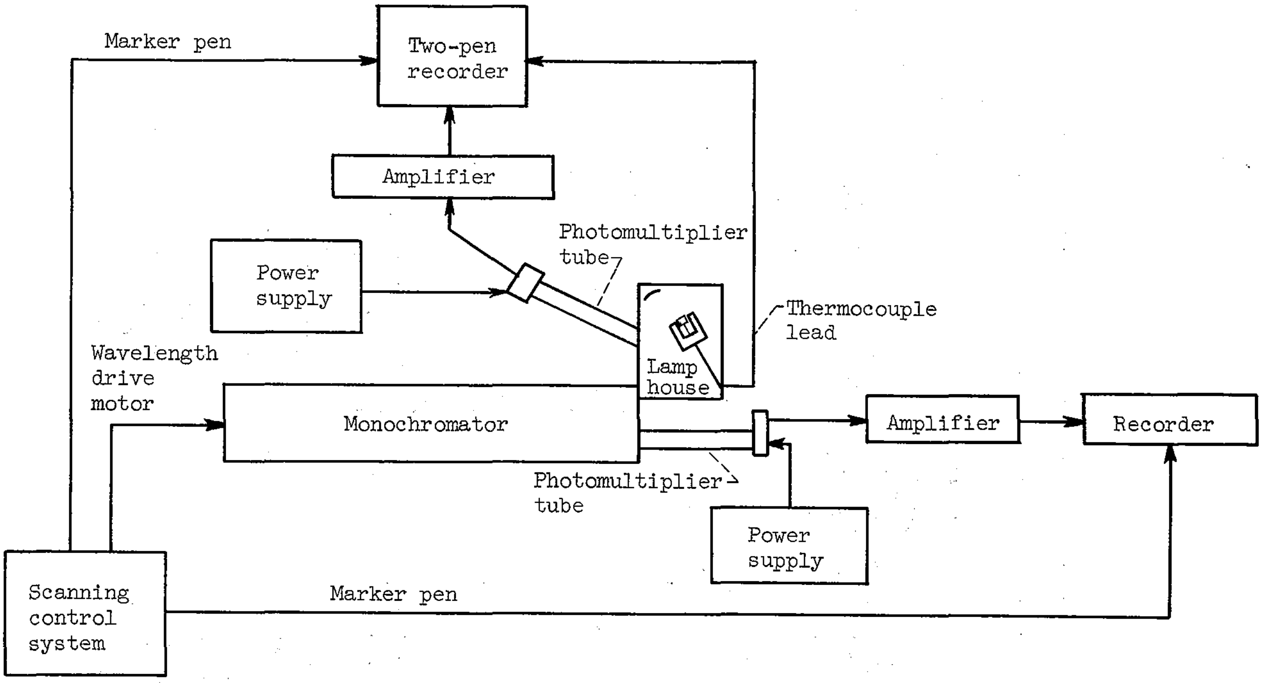


Figure 2. - Schematic diagram of recording apparatus.

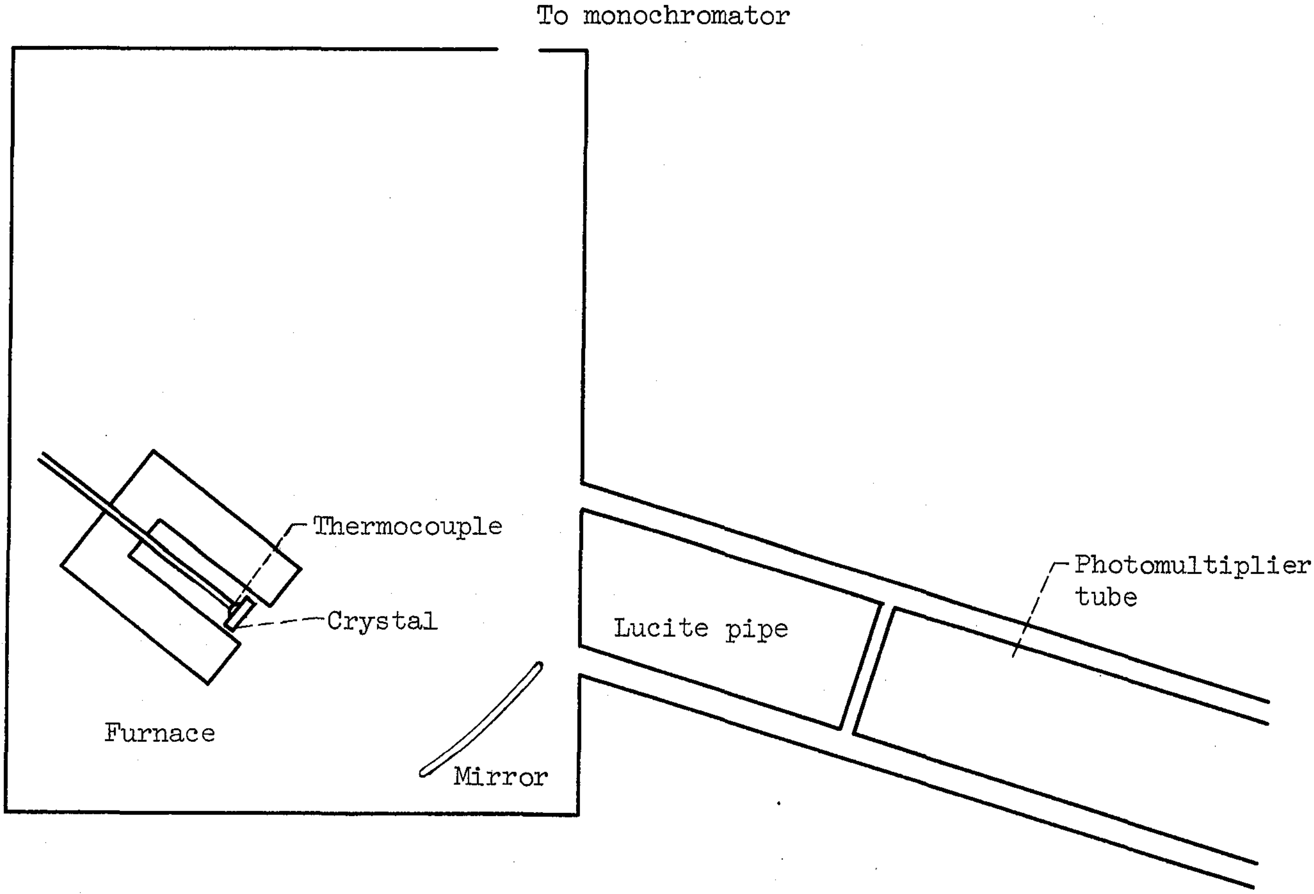


Figure 3. - Modified Beckman lamphouse.

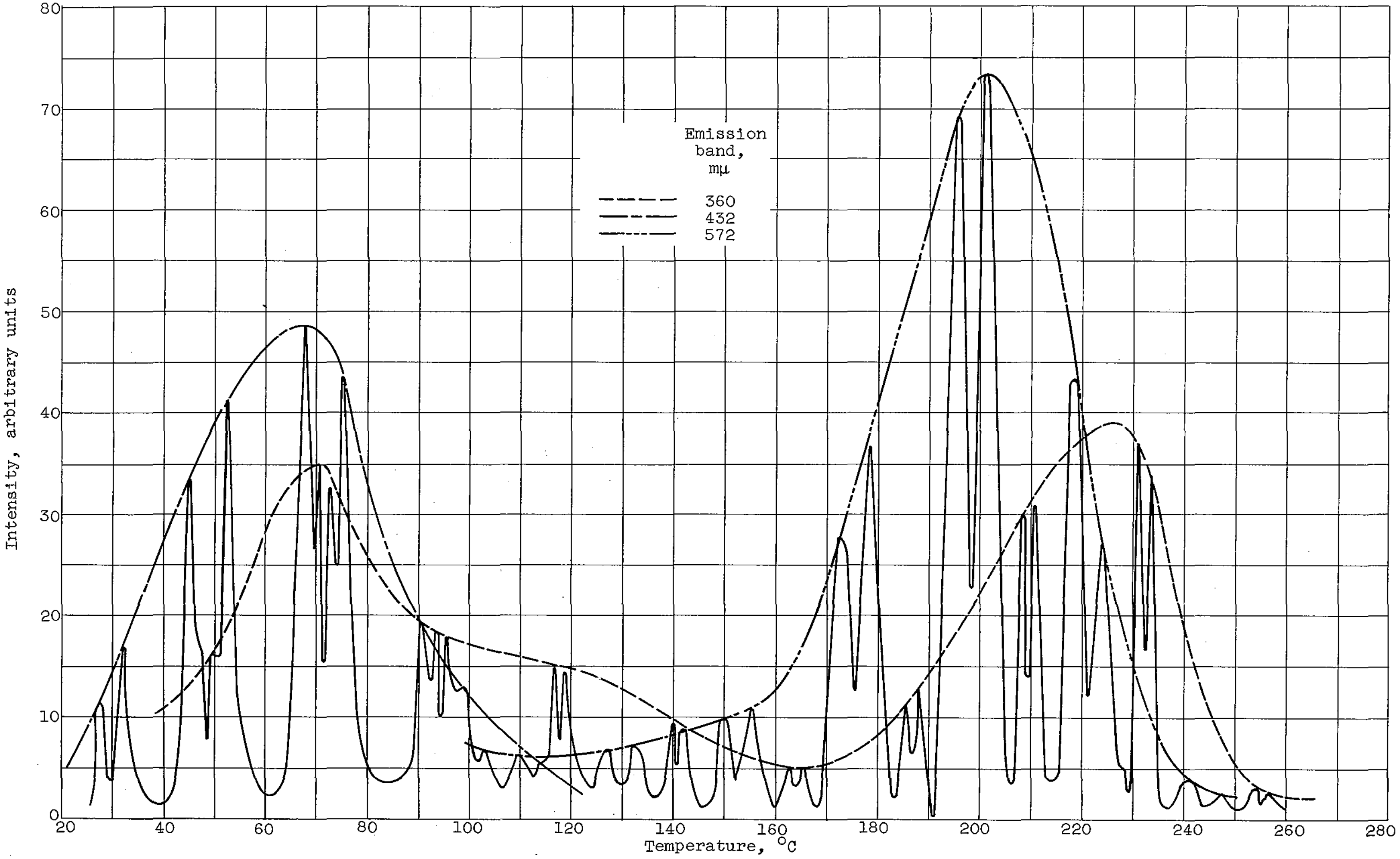
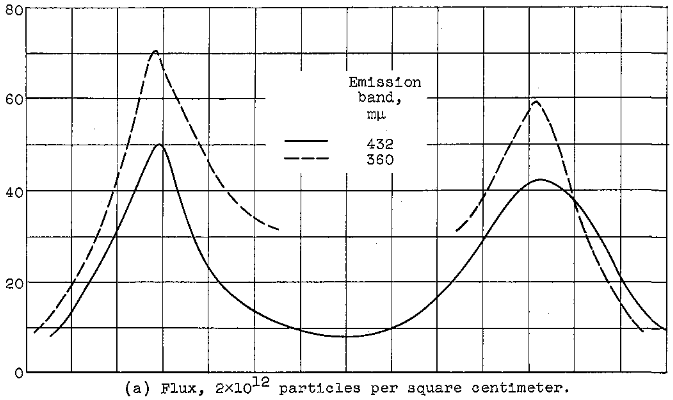
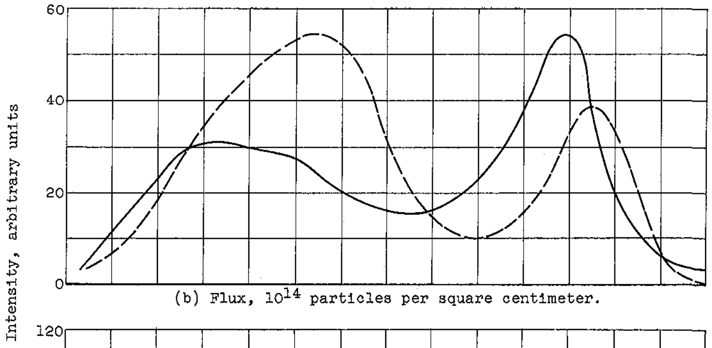


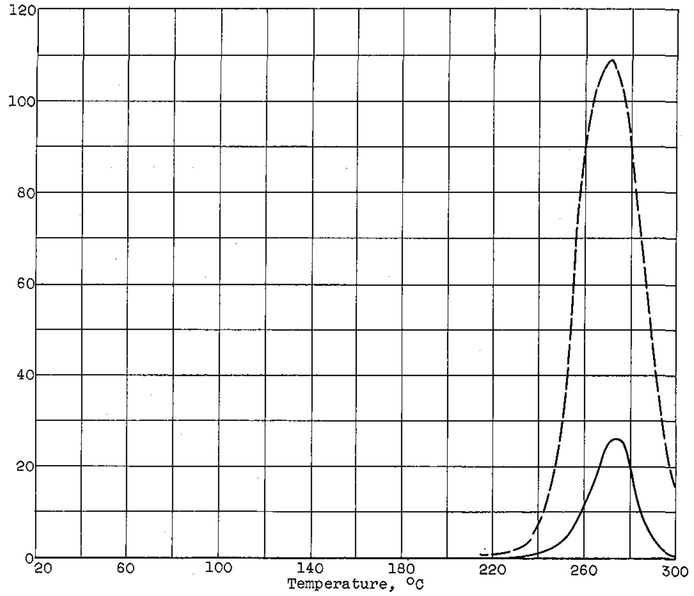
Figure 4. - Scan recording of spectra of hydroxide free crystal for flux of 10^{12} particles per square centimeter.



(a) Flux, 2×10^{12} particles per square centimeter.

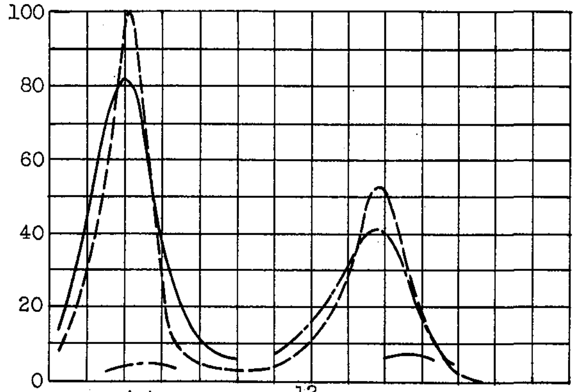


(b) Flux, 10^{14} particles per square centimeter.

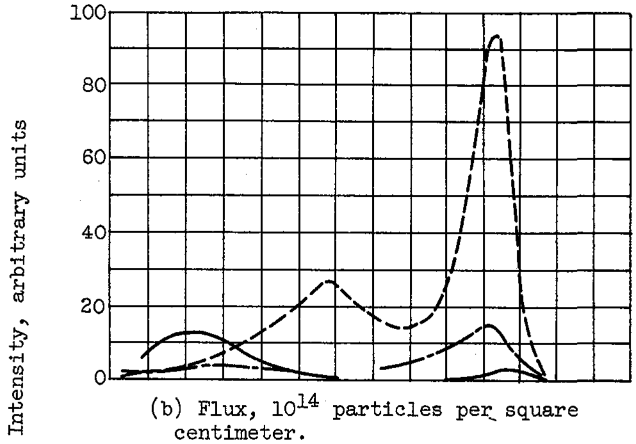


(c) Flux, 10^{16} particles per square centimeter.

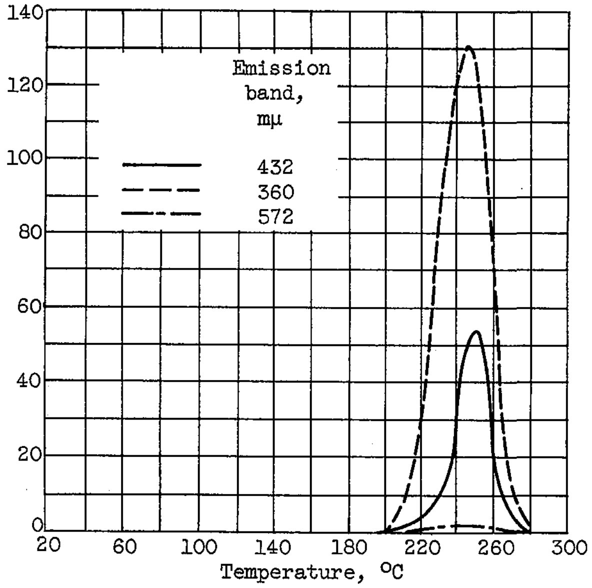
Figure 5. - Band glow curves of as-received crystal.



(a) Flux, 2×10^{12} particles per square centimeter.

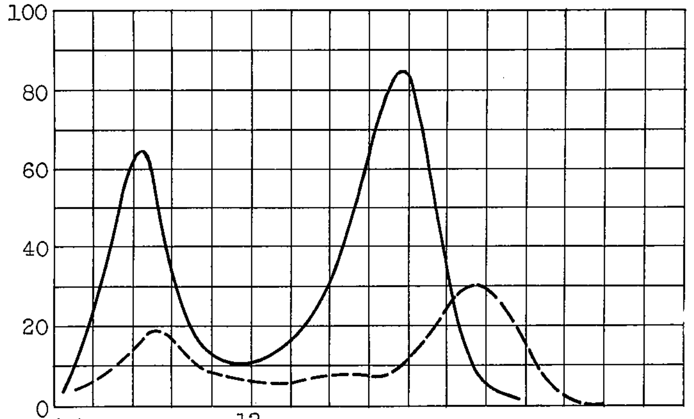


(b) Flux, 10^{14} particles per square centimeter.

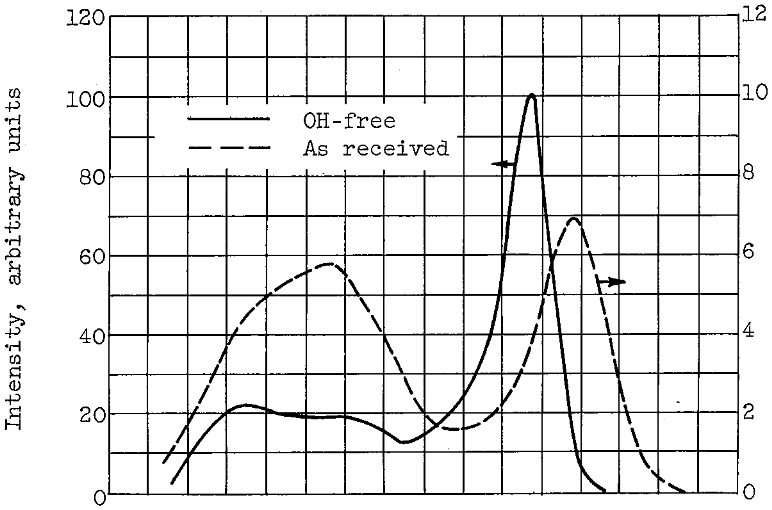


(c) Flux, 10^{16} particles per square centimeter.

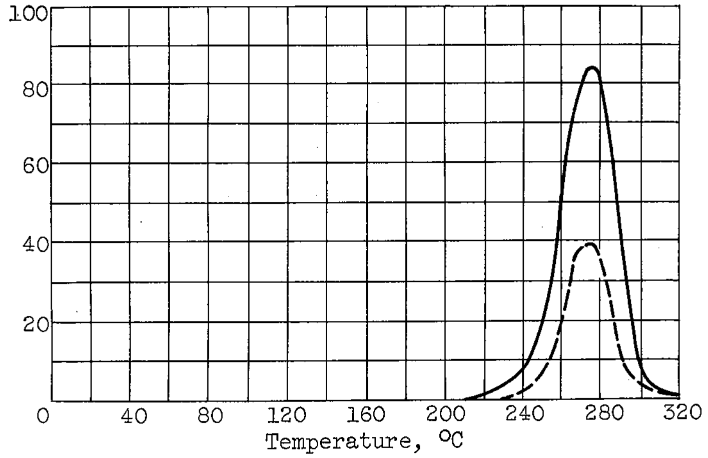
Figure 6. - Band glow curves of hydroxide free crystals.



(a) Flux, 2×10^{12} particles per square centimeter.



(b) Flux, 10^{14} particles per square centimeter.



(c) Flux, 10^{16} particles per square centimeter.

Figure 7. - Typical glow curves for hydroxide free and as-received crystals.

NASA-Langley, 1963