RED-LUMINESCING QUARTZ

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ABSTRACT

Red-cathodoluminescent quartz has been synthesized from amorphous silicic acid containing minor amounts of Al\textsuperscript{3+} and Mn\textsuperscript{2+}, in a reducing atmosphere at 1200° C. The emission spectrum shows a band extending from 5400 Å to >7000 Å, with a maximum at 6500 Å.

INTRODUCTION

During the course of investigating some luminescent glass systems, a red-cathodoluminescent coating was observed on the surface of certain high-silica glass samples. These were prepared in our laboratory by impregnating (Hood and Nordberg, 1943; Nordberg and Rumennapp, 1942; Nordberg and Rumennapp, 1944; Nordberg and Rumennapp, 1944) porous 96\% SiO\textsubscript{2} glass (Corning No. 7930) with a solution of a manganese salt and firing at 1200° C. in a reducing (H) atmosphere. The coating was white, and under excitation with a Tesla spark-coil showed red luminescence and some afterglow. The material was not excited by either 2537 Å or 3650 Å light. X-ray patterns (obtained with a 114.5 mm. cylindrical camera and CuKα radiation) revealed that the coating was composed of quartz with normal lattice spacings.

The existence of red-luminescing quartz raises several points of interest. (1) First, red-luminescing quartz has never been found in nature, with two doubtful exceptions (Peters, 1930; Saksena and Pant, 1951). (2) Recently, Feldman of the Naval Research Laboratory, working on an independent problem of luminescent thin films on glass, obtained a red-cathodoluminescent film of quartz by thermal evaporation in vacuo of a willemite phosphor (Feldman and O'Hara, 1958). (3) The anomalous generation of quartz at a temperature far above the normal stability range (870° C.) is not unprecedented. Several workers (Schulman, Claffy and Ginther, 1949; Bailey, 1949; Birks and Schulman, 1950) have reported the high-temperature formation of quartz from amorphous silicic acid in the presence of certain elements, such as Ca, which catalyze the reaction. The effectiveness of an aluminum-manganese (both are essential to red-luminescing quartz) combination, however, has not been known.

THE PHOSPHOR—COMPOSITION AND SYNTHESIS

Studies were made of the composition of the fortuitously-occurring material in the attempt to develop a method of controlled synthesis by conventional means. The presence of aluminum as well as manganese...
was determined to be essential to the phosphor composition. Aluminum is a minor constituent employed in preparing high-silica glass (Hood and Nordberg, 1940; Hood and Nordberg, 1940; and Hood and Nordberg, 1942). The original luminescent coating apparently resulted from the interaction of an aluminum-bearing glass with the manganese-solution. If the sample is prepared without aluminum (SiO₂:Mn only), the x-ray diffraction pattern obtained is predominantly that of cristobalite with only little quartz, and under spark-coil excitation the product shows dim pink emission and no afterglow. If prepared with aluminum alone (SiO₂:Al), only an amorphous material with weak white cathodoluminescence is obtained.

The phosphor is best prepared from amorphous silicic acid (Mallinckrodt’s “Special Bulky”) to which Mn^{12} and Al^{13} are added as aqueous nitrate solutions. The charge is dried, without mixing, under infrared radiation; fired in air at 1000°C for one hour; then ground and mixed with a mechanical mortar and pestle; and finally fired at 1200°C in an atmosphere of hydrogen for one hour. The preliminary air-firing serves to produce higher manganese oxides which mix more readily than the MnO₂ produced during drying. A reducing atmosphere is needed to assure the presence of divalent manganese. The firing temperature is quite critical—at 1100°C, a yellow-luminescing, probably amorphous, product is obtained; at 1250°C, the product is inert.

The optimum (molar) composition of the phosphor is: 0.90 SiO₂, 0.10 MnO, and 0.001 Al₂O₃. The possible range in activator concentration—of both manganese and aluminum—is very restricted. The upper concentration limit for MnO is approximately 0.10, whereas a lower concentration (0.05 mole) of MnO produces noticeably weaker and whiter emission. The luminescence of compositions containing more (0.005) or less (0.0005 mole) Al₂O₃ is less intense and decays much more rapidly than that of the phosphor of optimum composition. With the view to improving the brightness of the phosphor, several attempts were made to introduce more manganese and aluminum into the quartz lattice by means of fluxes, charge compensating cations, etc., but without success.

The phosphor preparations contain minor amounts of cristobalite and rhodonite (MnSiO₃), according to the x-ray diffraction patterns. MnSiO₃ is known to fluoresce at liquid nitrogen temperature under ultraviolet excitation. Its cathodoluminescence at room temperature, however, is negligible and does not contribute to the brightness of the phosphor. Moreover, the MnSiO₃ and any traces of amorphous silica which may be present are readily leached from the phosphor by treating it with 1% H₂F at room temperature for one hour. This effect no obvious change in emission brightness or color, although it slightly whitens the color of the
phosphor in reflected light. Digestion with 1% HF for as long as 14 hours, and solution of 80% of the sample, did not lead to preferential leaching of the cristobalite, although Sosman (1927) citing Schwarz (1912) reported a five-fold greater solubility for cristobalite as compared with quartz of uniform particle size. Differences in degree of crystallization and the distribution of the two minerals undoubtedly influence the extent of differential solubility. Since cristobalite is not known to luminesce, it should serve at most to dilute the phosphor and reduce its apparent brightness.

**Luminescence**

The phosphor is not excited by 2537 Å or 3650 Å ultraviolet. However, after exposure to x-rays (30 Kv, 15 ma) it phosphoresces salmon pink for several (5–10) minutes' duration, and is also excited to red luminescence and pronounced phosphorescence by 3650 Å; less so by 2537 Å excitation. The response to ultraviolet excitation after x-ray irradiation is a temporary property, and must represent an optical release, via the Mn centers, of energy trapped in the irradiated quartz. This phenomenon—radiophotostimulation—has not been reported previously for the quartz minerals. Audubert, Bonnemay, and Lautout (1950) described blue-white radiophotoluminescence in x-ray irradiated natural quartz. In the latter instance, the irradiation produced permanent centers, and the ultraviolet excitation could be repeated indefinitely.

The luminescence spectrum is reproduced as Fig. 1. It consists of a

![Emission spectrum, under cathode ray excitation, of red-luminescing quartz.](image)
broad band extending approximately from 5400 Å to beyond 7000 Å, and peaking at 6500 Å. The luminescence has an initial, exponential decay with a decay time of 8 milliseconds. These measurements were made under cathode ray excitation, using a phosphor sample that had been leached with HF. The phosphor also has a long-term afterglow, or phosphorescence, persisting (as detected by eye) for perhaps 5 minutes.

**Red-Luminescing Quartz**

The literature of mineralogy contains no reference to red-luminescing quartz. During a recent comprehensive study, Frondel and Hurlbut (1953) inspected some 1816 specimens of quartz and its varieties under 2537 Å and 3650 Å ultraviolet. A very few fluoresced, none red, and the fluorescence was in all cases attributed to foreign inclusions and not to the quartz itself. X-ray irradiation of natural and fused quartz excites blue-white fluorescence and phosphorescence, and also produces radiophotoluminescence in response to 2200–5500 Å excitation, according to Audubert et al. (1950).

J. T. Randall (1939), on the other hand, reported that silica (crystalline state not specified) prepared with 100 p.p.m. manganese by heat treatment at 1400° K. luminesced (4450 Å?, 5600 Å emission bands) under spark-coil excitation at low temperature (90° K.), but that the red emission band of manganese appeared to be missing. At room temperature, only a broad continuum was seen.

Saksena and Pant (1951) reported that the cathodoluminescence of quartz is so feeble that 70,000 V cathode rays and a 6-hour (spectrographic) exposure were necessary to obtain the spectrum, which consisted of two bands, at 3000–4900 Å and 5650–6550 Å. They were inclined to believe that the long wavelength band corresponded to the red cathodoluminescence observed by Peters (1930) and may have been associated with the Si-O bonds in quartz or with F centers produced by the intense irradiation. Certain early workers—Goldstein (1907); Peters (1930)—studying vacuum tube discharges, observed red-fluorescing areas on the tube walls (glass, fused quartz, rock crystal). Peters, using low-voltage cathode rays and 50-hours' spectrographic exposure, obtained a spectrum from pure quartz which consisted of a band at 5895–7238 Å (max. at 6338 Å and 6425 Å) as well as bands in the green (5600 Å) and blue (4790 Å). The red fluorescence disappeared, however, after 70 hours of operation. Peters attributed the fluorescence to the SiO₂ group.

We have examined a few random specimens of quartz with a spark-coil and have found no cathodoluminescence in any. These included rose quartz (Bedford, N. Y.), amethyst (Patterson, N. J.), smoky quartz (locality unknown), drusy quartz associated with pyrite crystals (Lead-
ville, Colo.), crystals from sandstone (Arkansas), and crystals intergrown with hematite (Elba or Frizington?). Synthetic crystals, grown by the Squier Signal Laboratory, Fort Monmouth, N. J., also were inert for the most part, although some had weak blue cathodoluminescence.

It is believed that the red-cathodoluminescent film obtained by Feldman and O’Hara (1958) by evaporation by $\text{Zn}_2\text{SiO}_4: \text{Mn}$ or from $\text{SiO}_2$ plus manganese, and identified by x-ray diffraction and infrared reflection spectra as quartz, developed by a reaction with traces of aluminum in the Vycor glass substrate, and is comparable to the independently prepared phosphor, quartz: $(\text{Mn} + \text{Al})$, discussed in the present paper and briefly described elsewhere in a Letter to the Editor (Claffy and Ginther, 1959).

**Manganese and Aluminum Impurities**

Linwood and Weyl (1942) have postulated that the red luminescence of manganese in certain silicate glasses and crystalline compounds may be due to interstitial $\text{Mn}^{++}$, in 6-fold coordination. Buerger’s work (1948) has indicated, however, that only an ion such as $\text{Li}^{+}$ (0.60 Å) is small enough to enter the quartz lattice, and that large ions (Na+, 0.95 Å) can occur only in the cristobalite-type structure. Although $\text{Mn}^{++}$ (0.80 Å) is intermediate in size, its charge is greater. Manganese is a rare impurity in natural and synthetic quartz. For example, in ten published spectrographic analyses of quartz, manganese is reported by Cohen and Sumner (1958) as “not found”; and of seven analyses of amethyst (Cohen, 1956), manganese was “not found” in two and its concentration in the other five never exceeded 0.006%. Frondel (1952) reported ten chemical analyses of quartz. Manganese was not found in four; in the remaining six, the highest concentration was 0.00005%. Furthermore, in the growth of synthetic quartz it has been the experience at the Squier Signal Laboratory (J. M. Stanley—private communication to G. W. Arnold, Jr., of NRL; Feb. 20, 1957) that manganese could not be incorporated into the growing crystal.

It is therefore of interest to consider the present case of the phosphor, quartz: $(\text{Mn} + \text{Al})$, where optimum luminescence is obtained upon the addition of 10 mole% manganese. We must assume, on the basis of the known behavior of manganese in relation to natural and synthetic quartz, that only some few thousandths of a per cent manganese has been incorporated into the quartz lattice. It may be that in the presence of the aluminum, slightly more manganese can enter the crystal. Probably another, greater, percentage of the manganese has entered the cristobalite since the cristobalite structure is open and readily accommodates large ions (Buerger, 1948; Linwood and Weyl, 1942; Barth and Posnjak,
By chemical analysis it was determined that the leached phosphor—i.e., quartz+cristobalite, actually contained 1.5% (wt.) manganese and the crude, unleached phosphor contained 22.5% MnSiO₃. Of the initial quantity of manganese used in synthesizing the phosphor, therefore, 96% formed MnSiO₃ and only 4% was incorporated into the quartz and cristobalite lattices. We are forced to conclude, then, that the bulk of the manganese must be fixed as rhodonite in a favored, competing reaction. It is not clear, otherwise, why such a great excess of manganese should be necessary to obtain the phosphor.

Aluminum, in concentrations of 0.0001 to 0.01%, is a common impurity in quartz (Frondel, 1952), and is known to substitute for Si⁴⁺ in the tetrahedral network of quartz and silicate minerals, the charge imbalance being generally compensated by interstitial alkali ions. Perhaps (Al+Mn) form a similar charge-compensating pair in the quartz phosphor; chargewise, 1 Mn²⁺ could compensate for 2 Al³⁺ ions.

Cohen and Sumner (1958) elaborated the thesis that aluminum can occupy interstitial as well as substitutional positions in the quartz lattice, and that interstitial impurities expand only the a lattice direction markedly, whereas substitutional impurities affect both axes. Our x-ray diffraction data for the red-luminescing quartz phosphor are not of sufficient precision to distinguish the small lattice changes involved. Quartz containing interstitial aluminum only is said not to develop the 4600 Å absorption band even after extensive (3.8×10⁸ r) x-ray irradiation (Cohen and Sumner, 1958). A phosphor sample subjected to approximately that dosage by irradiation in a Van de Graaff generator showed slight discoloration. This result in itself is inconclusive since absorption measurements could not be made on the phosphor-powder.

It may be argued that the Mn-bearing cristobalite is actually the active, luminescent phase and inability to separate the quartz from the cristobalite leaves identification of the phosphor unsettled. The following facts are convincing, although indirect, evidence that the phosphor is indeed quartz. (1) The fortuitous luminescent coating on glass is quartz only. (2) The luminescent thin film prepared by Feldman is quartz only. (3) The characteristic red emission is obtained only when (Mn+Al) are used to prepare the phosphor, in which case the x-ray diffraction pattern shows predominantly quartz. When manganese alone is used, the product is inert and the x-ray diffraction pattern shows cristobalite predominating.

Acknowledgments

We are greatly indebted to Dr. C. C. Klick for the measurements made under cathode ray bombardment, and to Dr. J. H. Schulman for
many discussions and suggestions. Mrs. Evelyn Cisney assisted in the x-ray diffraction investigation of the acid-leached material.

**REFERENCES**


Manuscript received December 12, 1958.