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A unique green quartz

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Abstract

Some unique green quartz, collected by Dana in Brazil in 1884 (NMNH 44678), was examined. The green color, due to a broad absorption band at 2eV and a strong band extending from 2.5eV into the ultraviolet, is lost by heating to 500°C, and cannot be recovered by irradiation or by heating under reducing conditions. The usual amethyst color (absorptions at 2.3 and 3.5eV) can be obtained by irradiation and is lost at 350°C. Some amethyst coloration is also present with the original green. The two colors can coexist or exist independently of each other. Chemical analysis shows 0.037 to 0.100 percent Fe, 0.022 to 0.029 percent Al, and 0.003 percent to 0.004 percent B. The exact cause of the green color has not been established.

During an examination of almost 400 natural and synthetic quartz specimens for their behavior with respect to irradiation and heat, some green material collected by E. S. Dana in Brazil in 1884 was found to be unique. It is in the Smithsonian Institution (NMNH 44678), and consists of five yellow and two green 1 to 2 cm crystal fragments.

One of the yellow specimens, designated 44678C, was examined and found to be a typical citrine, containing 0.0*X* Fe and Al, 0.00*X* Ca, all other elements detectable by emission spectroscopy being 0.000*X* percent or lower. When irradiated, part of the specimen showed amethyst characteristics; presumably the same is true of the other four yellow pieces.

Both green pieces, designated 44678A and B, were analyzed and found to contain respectively 0.10 and 0.037 percent Fe, 0.029 and 0.022 percent Al, 0.004 and 0.003 percent B; both had 0.00*X* Ca and 0.000*X* Mg; all other elements were less than 0.000*X* percent. Crushed and acid-washed samples were run by emission spectrochemical analysis with accompanying reference standards to give a precision better than 10 percent.

Polarized spectra were obtained on a Cary 14R spectrophotometer. Only the π spectra (extraordinary ray, E parallel to c) are presented; the σ spectra are similar but show less detail.

The spectrum of part of specimen 44678A is shown in Figure 1 in the as-received form, *A*. After γ-irradiation with 15 megarads from Co-60, the additional absorption in Figure 1B corresponds to an amethyst coloration superimposed on the green. This absorption disappeared on heating to 350°C with a return to the original green color. In a crystal 0.5″ thick, this green color corresponds to No.. 102, medium greenish yellow (Kelly and Judd, 1975).

Heating another section of this crystal to 500°C resulted in a loss of the green color, Figure 1C. Subsequent irradiation again produced amethyst, Figure 1D, without, however, restoring the green. This amethyst color was also lost on heating to 350°C. A fragment of 44678B showed the same sequence of color changes as 44678A.

The two colors, green and amethyst, are thus completely independent of each other, and the difference curves of Figure 2 show the characteristics of each. The amethyst component (Fig. 2a) is seen to originate from the transmission bands in the red (below 2eV) and blue-violet (about 2.7eV) derived from the usual amethyst absorptions near 2.3 and 3.5eV (5400 and 3500A, respectively) (Lell *et al.*, 1966, who summarize early work on quartz). The green component (best analyzed from Fig. 2b, A–C) originates from a relatively weak transmission in the blue-green (about 2.4eV) resulting from a broad absorption band at 2eV and a strong band or series of bands starting rather sharply at 2.5eV (4950A) and extending into the ultraviolet. It is destroyed by heating to 500°C and cannot be recovered by γ-irradiation.

This green quartz appears to be quite distinct from

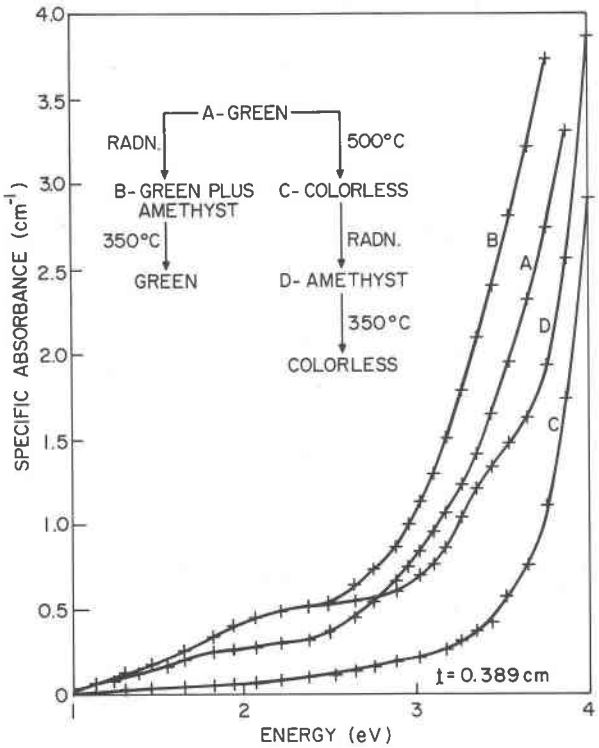

Fig. 1. The π absorption spectra (extraordinary ray, E, parallel to c) crystal No. 44678A in as-received form (curve A) and after the treatments indicated (curves B, C, and D); Radn. indicates Co-60 γ-ray exposure of 15 megarads.

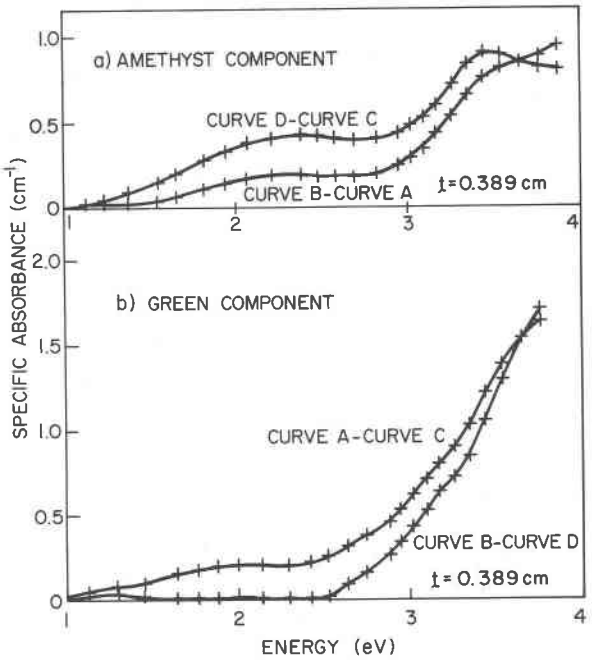

Fig. 2. Difference curves for the spectra of Fig. 1.

"greened amethyst" (*e.g.* Lehmann and Bambauer, 1973), from the "greenish-yellow" quartz (Samoilovitch *et al.*, 1968; Lehmann, 1971; Lehmann and Bambauer, 1973; Nassau and Prescott, 1975; Nassau and Prescott, in preparation) and from the other green colors recently reported in synthetic quartz (Nassau and Prescott, in preparation).

These experiments do not establish whether this unique green color is due to a growth-formed color center not reproduced by γ-rays, due to the presence of Fe in an unusual crystal site (with decoloration from heating resulting from ionic motion or from valence change), or possibly related in some way with the unusual boron content. Detailed resonance work will be required to establish the exact origin of this green color. Heating in hydrogen did not prevent the loss of green color, nor was the color recovered at temperatures as high as 800°C. This color and the associated absorption spectrum do not appear to have been previously observed in either natural or synthetic quartz.

This work was made possible by the loan of specimens by J. S. White of the Smithsonian Institution; they have been returned: 44678A and 44678B in colorless, green, and amethyst states; and part of 44678C in the amethyst state.

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