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LIGHT SCATTERING OF HEAT-TREATED QUARTZ IN RELATION TO HYDROGEN-CONTAINING DEFECTS[1]

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ABSTRACT

Certain quartz crystals become milky after heat treatment. The local intensity of milkiness is related to the local intensity of the 3μm absorption band and hence is related to the H content. Infrared combination bands reveal the formation of network in accordance with the reaction $2\equiv Si-OH \rightarrow \equiv Si-O-Si\equiv + H_2O$. The scattering regions are assumed to consist mainly of H_2O-containing cavities and micro-discontinuities formed from "gel defects" during experimental annealing. Spectrochemical analyses indicate that alkali aluminum silicate precipitates are not the main cause of such milkiness.

INTRODUCTION

Some quartz crystals become milky after being heat treated, *e.g.* at 550°C for a few days or at 700°C for a few hours. These include both synthetic crystals grown on "unnatural" planes, *e.g.*, grown along [0001], and natural crystals that show the peculiar pattern of lamellar *r-l*-twinning common in amethysts (Frondel, 1964, p. 171–181; Schlössin and Lang, 1965). Various models may be advanced to explain the formation of scattering regions: (1) precipitation of alkali aluminum silicate phases taking up trace elements as suggested by Cohen and Hodge (1958), Cohen (1960), Bastin and Mitchell (1962); (2) voids as found by Arnold (1960) in spinels formed by diffusion, especially of O vacancies; (3) "submicroscopic liquid inclusions" as assumed by Brown *et al.* (1962) to cause Tyndall scattering in synthetic quartz (not annealed); (4) "gel defects" and "bubble" mechanisms suggested by Brunner, Wondratschek and Laves (1961).

In this paper further support is given to the last mentioned assumption. "Gel defects" are a special type of H-containing defects of which Brunner *et al.* (1961) and to some extent also Kats (1962) recognize three main types: *Type (a):* "AlH" stoichiometrically replacing Si, with Al^{3+} at an Si^{4+} site and H^+ bond as OH^-. *Type (b):* M OH- "molecules" at interstitial sites ($M = Li^+$, Na^+). *Type (c):* "gel-like" regions with a high local concentration of H_2O and/or Al/Si tetrahedra with one or more OH groups attached in a locally disordered network. These three types have

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[1] The results of this paper have been presented by F. Laves at a "Gordon Research Conference", Meriden, N.H., USA, June 1964.—Since then, papers by Dodd and Fraser (1965, 1967) and by McLaren and Phakey (1966) appeared treating similar subjects.

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different properties. Types (a) and (b) cause several sharp and polarised absorptions in the 3μm region. The OH bonds are perpendicular to the *c*-axis of quartz and the H sites are structurally well defined (though not known in detail). When annealed above about 650°C, the defects (b) disappear by forming more defects (a), the OH group of MOH presumably filling oxygen vacancies. In clear, natural quartz crystals these first two types (a) and (b) are the predominant "chemical" defects (Bambauer 1961; Bambauer *et al.*, 1961, 1962, 1963). Defects of type (c) cause a broad unpolarised 3μm absorption indicating a continuous variety of bridging H sites. The relative abundance of H_2O and SiOH groups can be estimated from combination bands at 1.9 and 2.2μm (Scholze, 1960). When annealed above about 500°C the amount of SiOH (if predominant before) decreases and that of H_2O increases. Electrolysis of quartz with inert electrodes results in a replacement of the alkalis by hydrogen which may be taken up from atmospheric H_2O (Wondratschek *et al.* 1960) or from purposely added H_2 (Pfenninger 1961).

EXPERIMENTAL

Milky precipitation has only been observed in natural or synthetic crystals predominantly showing an OH absorption band of the gel type listed above under (c). No crystal became uniformly milky over areas larger than a few mm^3; the distribution followed growth zones and sectors.

Figure 1 shows (a) the optical density of a *basal growth* synthetic quartz at the wavelength of 0.450 μm which has been γ-irradiated; (b) the optical density of the crystal at the peak wavelength of the OH absorption ($\lambda = 2.45$ μm) as a measure of the local concentration of H (this absorption remained practically unchanged by γ-irradiation and annealing); (c) the optical density of the annealed crystal at the wavelength of 0.350 μm as a measure of the local concentration of scattering regions; (d) the photograph of the annealed crystal showing the milky precipitation. The optical density curves were obtained by moving the crystal through the spectrometer beam near its focus. For curve (b) the crystal could be moved directly through the focal point; hence the spatial resolution is best in this curve. The thickness of the specimen was 10 mm for curve (a), and 2.5 mm for the others.

Figure 2 shows the average concentration of the main trace elements in four regions (indicated by arrows) of a section of the same crystal as shown in Figure 1. Li, Na and Al were determined by emission spectroscopy; for details see Bambauer (1961). The H concentrations are mean values of those calculated from peak and integral absorption of the 3-μm band using the absorption coefficients of liquid H_2O as discussed in the paper by Brunner *et al.* (1961). The H concentrations are believed to lie within a limit of error of the factor 2.

At the bottom of Figure 2 is shown an autoradiograph of the neutron activated crystal. The radiation is due to Na^{24} as checked by decay time and γ-spectroscopy. This photograph provides qualitative confirmation of the result of the Na analysis, as given in the upper part of Figure 2.

The correlation between local H concentration and milky precipitation has also been indicated by a radiograph of a natural lamellar *r*-*l*-twinned crystal which has been annealed in a tritium containing atmosphere.

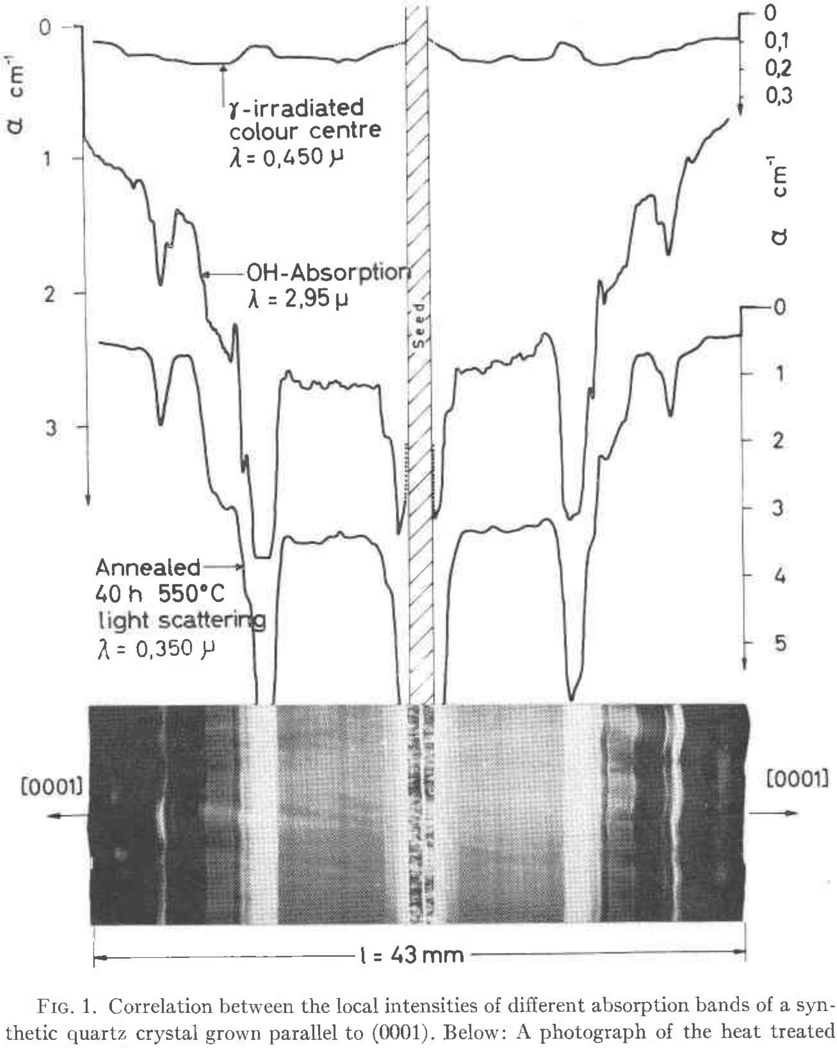

FIG. 1. Correlation between the local intensities of different absorption bands of a synthetic quartz crystal grown parallel to (0001). Below: A photograph of the heat treated crystal showing white regions of Tyndall scattering.

DISCUSSION

Obviously there is a correlation between the local concentration of scattering regions and of H and Na, whereas Al and Li behave differently and are present in minor quantities only. Therefore, the scattering is not primarily due to the precipitation of an alkali aluminum silicate. The measured concentration of Na compared to that of H (see Fig. 2) is about 100 to 10 times higher in the crystal than in synthetic growth solutions

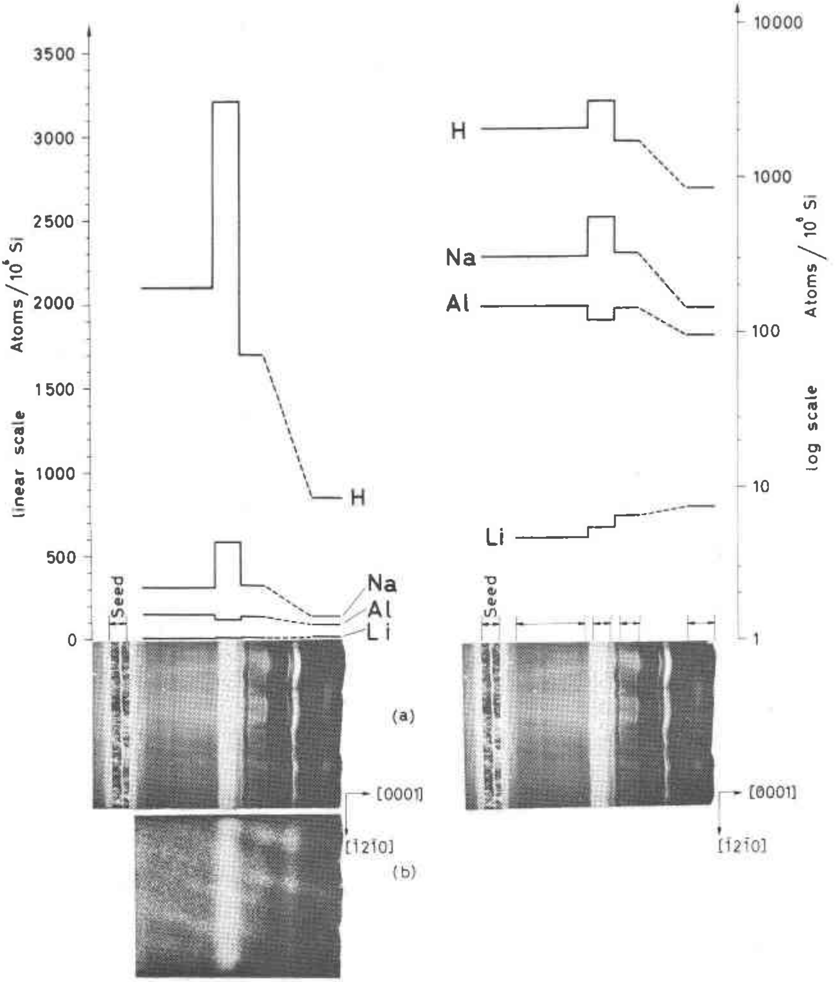

FIG. 2. Average trace element concentrations in four regions of the crystal shown in Fig. 1. (a) The same photograph as shown in Fig. 1. (b) An autoradiograph showing the Na-distribution qualitatively. (The radiating Na-rich regions of the neutron activated crystal appear white in the photograph.)

such as 0.1 to 1 n NaOH. It is unlikely, therefore, that the trace element content is mainly due to bubbles of mother liquid included during growth.

Since the paper by O'Brien (1955) the brownish colour of "smoky quartz" is generally believed to be connected with (Al, Si) substitution. In principle, such a correlation is shown up here. This correlation is known to have exceptions, *e.g.* if the (Al, Si) substitution is compensated by protons (Bambauer, 1961; Pfenninger, 1961).

The following model for the scattering regions seems a likely one: under special growth conditions H_2O and SiOH (tetrahedra with one or more OH groups) together with Na^+, NaOH, Al^{3+} . . . are taken up in a locally disordered and probably less dense network. We use the term "gel-like region" as a practical and short description of this kind of defect. When heat-treated under atmospheric pressure, the "network" linkages are increased. Insofar as there is no sterical hindrance, the OH groups will react schematically as follows: $2{\equiv}\text{Si-OH} \rightarrow {\equiv}\text{Si-O-Si}{\equiv} + H_2O$ (Brunner *et al.* 1961, particularly Fig. 9 and footnote 62). The gel regions may transform into a more dense "glassy" structure, rich in trace elements, and into cavities in which H_2O is enriched. H_2O may locally develop sufficient pressure to cause the formation of cavities by plastic flow. As to the formation of cavities within a "sound" crystal, see Mollwo (1941), Mollwo and Pohl (1941). Furthermore, microfractures starting from the bubbles may provide additional space. They may elastically close when the crystal cools down. Hence the scattering power as measured at room temperature approaches a saturation value which is only slightly increased with increased annealing temperature (the observation of a saturation has been interpretated by Bastin and Mitchell, 1961, as an argument against the idea of water bubbles). Presumably many varieties extending from real "bubbles" to "local sponge texture" are formed, and their size and relative abundance may vary in different crystals and in different parts of the same crystal. The rate of growth of these "particles" is influenced by the formation and diffusion of H_2O. On this point, our model and some of the assumptions on a "thermally activated migration of impurity atoms" by Bastin and Mitchell agree in principle. We do not exclude the possible contribution of other defects and trace elements.

Electrolysis (H replacing Na) appears to favor the formation of H_2O bubbles: from diagrams by King (1960) it can be seen that some properties of synthetic crystals undergo a significant change in the range between 0° and $-20°C$ which might be explained as the freezing of (purified) H_2O bubbles. In view of the acoustic damping and milky appearance King suggested the formation of a network by the growth of devitrified aggregates (sodium aluminum silicate).

Several authors have reported on tendencies for different amounts of trace elements to be taken in different zones and sectors of synthetic quartz material (reviewed by Frondel 1962, p. 68–70). The indications are not unambiguous, however. "Unnatural" seed planes build up "natural" planes, as for instance when basal seeds build up growth hills with a tendency to become rhombohedral faces. The intersections of such hills, the discontinuities on them as well as the twin boundaries in crystals with *r-l*-twinned lamellae, seem to be favored regions for gel-defect formation. Hence, the number and the geometry of these hills influence the development of a crystallographic surface and the growth mechanisms vary in an uncontrolled manner during synthesis. This may be one of the reasons for the nonuniform appearance of such crystals. In a growth experiment by O. W. Flörke (1962) a seed inclined 7° to a rhombohedral plane was used, part of the seed preserved the inclined face and grew with the formation of "hills", part turned into the rhombohedral plane with a "flat" surface. The hilled region showed a stronger 3 μm absorption of the gel type than the flat region.

We believe that the scattering particle model described here, and an equilibrium dependent on pressure and temperature between H_2O and $\equiv$Si-OH in gel-like defects, are of general importance for the appearance of natural silicate minerals. Further, it might explain the influence of "fluxes" on phase transformations of feldspars (see Laves, 1950 and 1952; more specifically Donnay, Wyart and Sabatier, 1960). The bond breaking action of "water" has been used by Griggs and Blacic (1965) to explain the remarkable weakness of synthetic quartz.

The correlation between milky appearance and H-content has also been observed in zircon. The amount of H and the relative abundance of H_2O and OH groups in zircons seem to be "fingerprints" of geological events (Grünenfelder *et al.*, 1963, 1964, and forthcoming papers). Further work is needed to understand fully the various kinds of H containing defects.

Clear natural quartz crystals (except those with *r-l*-twinned lamellae common in amethysts) are practically free of the gel-defects dealt with in this and the earlier papers quoted. For a discussion of other H-containing defects see Brunner *et al.*, (1961), Kats (1962), Bambauer *et al.*, (1962).

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