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Distribution of OH in Synthetic and Natural Quartz Crystals

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The relative intensities of different OH vibration bands have been studied in synthetic quartz crystals with total OH concentration varying by more than a factor of 30 by means of infrared absorption measurements at 78°K. Local variations of OH concentration also have been measured for different directions in these samples and in two crystals of natural quartz from Brazil. Integral absorptions of the different bands in the 3400 cm^{-1} region were all found to increase linearly with total OH concentration. Therefore, mechanical Q could be related to any one band of the spectrum as well as to the total OH concentration. Since for natural quartz no relation between total OH concentration and mechanical Q seems to exist, the effect of OH defects characteristic for synthetic quartz must be high, while the OH defects characteristic for natural quartz (i.e., rock crystals and smoky quartz) have a small effect on the mechanical Q.

OH concentrations in the Z- and $+X$-zones were found to be lower near the edge than near the seed. The concentration of OH varies in the order $Z < +X \ll -X$, suggesting that OH acts as a charge compensator for metal impurities, notably Al^{+3}. In natural quartz, the OH concentrations near the edge were also lower than in the interior parts. The overall differences for different directions were much smaller than in the case of synthetic quartz.

I. Introduction

The series of sharp absorption bands in the near infrared 3400 cm^{-1} region of α-quartz has drawn the attention of several workers (*1–6*). Kats (*2*) was able to show that these bands are due to vibrations of OH groups associated with various types of lattice defects. With exchange of hydrogen against deuterium, Kats observed band shifts into the 2600 cm^{-1} region, as expected due to the change in reduced mass. Bambauer (*4*) measured OH concentrations in natural quartz. He also showed that the extinction coefficients of some bands, individually or in combination with those of other bands, increase approximately linearly with total OH content of the crystals. He used samples from different locations in the Swiss Alps. Wood (*1*) qualitatively observed intensity variations of the infrared absorption bands in a synthetic quartz crystal. However, distribution of OH in different growth regions of the same sample has not yet been measured quantitatively, and in the case of synthetic quartz, systematic measurements for crystals with different mechanical Q values are still lacking. Therefore, we thought it necessary to measure OH concentrations in synthetic quartz crystals and the variation in different growth zones (Z, $+X$, $-X$) of each of these crystals quantitatively, in relation to their mechanical Q.

Mechanical Q was found to be dependent on extinction coefficient (α) at 3585 cm^{-1} by Toyocomm (*7*) and at 3500 cm^{-1} by Dodd *et al.* (*3*). and Sawyer (*8*; in the case of synthetic quartz). The International Electrotechnical Commission (*9*) also recommended a Q versus α_{3590} curve[1] as a method for determination of the Q-factor.

In the present work, we attempted to find a relation between integral absorption of the

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[1] This band shifts to 3585 cm^{-1} from room temperature to 78°K (*2*).

3585 cm^{-1} band and others with the total infrared absorption, in the 3400 cm^{-1} region, i.e. the total OH concentration. The results of such an investigation were expected to give an indication whether a single OH defect, a combination of several or the sum of all OH centers causes the decrease of mechanical Q.

II. Experimental

The synthetic crystals under investigation were grown hydrothermally. The growth conditions and their effects on average mechanical Q of most of the crystals studied in this paper have already been published (*10*).

The samples were plates with thicknesses between 2 and 5 mm, depending on OH concentration of the crystal, sectioned perpendicular to the Y-axis of quartz, ground, and polished carefully. Care was taken to avoid the natural face cappings of the crystals, since these face cappings are known to be covered by a very imperfect growth layer (*11*). The Q-factor was determined from the Q–α_{3590} curve of Toyocomm (with α values measured at room temperature).

Infrared spectra were recorded at 78°K with a Grubb Parsons Spectromajor Spectrometer of maximum resolution of 0.3 cm^{-1} employing two interchangeable gratings. Samples were mounted in a cryostat so that the light beam passed perpendicular to the Z-axis. The area of the sample exposed to the light beam was about $3 \times 5\ \mathrm{mm}^2$. The average sample size was $25 \times 15 \times 4\ \mathrm{mm}^3$.

The OH concentration was calculated from the integral absorption using the relation

$$C = \frac{\int E d\bar{\nu}}{d} \cdot \frac{f}{\varepsilon'} = 2.11 \cdot K\,[\mathrm{OH}/10^6\,\mathrm{Si}]$$

for unpolarized light, where K = integral absorption = $\int E d\bar{\nu}/d$, d = thickness of sample (cm), $E = \log\ I_0/I$ = absorbance, $\varepsilon' = \frac{2}{3}\varepsilon_m$, ε_m = 14 000 cm/g-atom = molar absorption coefficient for integral absorption (*4*), $\frac{2}{3}$ = anisotropy factor, $f = \rho \cdot 10^6/60$; $\rho = 2.66$ g/cm^3 = specific gravity of quartz.

In contrast, Kats has used the relation $N = 2.16 \times 10^{16} \cdot K/\mathrm{cm}^3 = 0.81 \cdot K/10^6$ Si for unpolarized light incident perpendicular to the Z-axis as in our case. Kats (*2*) assumed orientation of the OH dipoles perpendicular to the Z-axis. Actually, the OH dipoles make various angles with the Z-axis. Their effect is already included in the experimental ε_m value. Therefore we used the formula given by Bambauer (*4*).

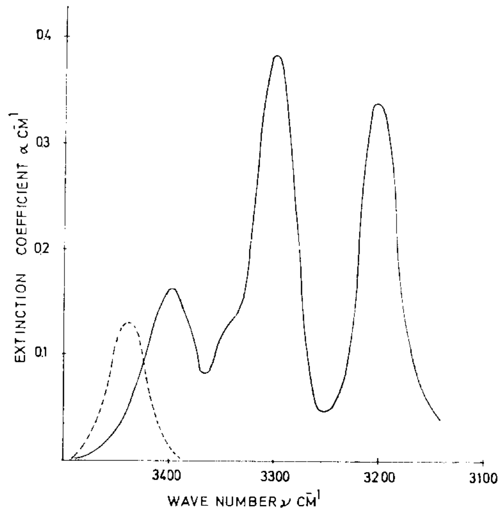

FIG. 1. Infrared absorption of α-quartz in the 3200 to 3800 cm^{-1} region, excluding OH vibration bands. Solid curve from (*2*); dashed curve from this work.

The OH vibration spectra in the 3400 cm^{-1} region are always superimposed by overtone and combination bands of the SiO_2 lattice (*2*). Figure 1 is an enlarged reproduction of the Si–O vibration spectra in the region between 3200 and 3800 cm^{-1} for a quartz free from OH according to Kats (*2*; solid line). The integral absorption values for Si–O vibration bands at 3204, 3300, 3355, and 3400 cm^{-1} were determined from Fig. 1 and are K = 15, 17, 5, and 9 cm^{-2}, respectively. The experimental absorption spectra were corrected for this lattice absorption. OH concentrations and Q-factors were determined in the Z-zone, near the edge (*1*), near the seed (*3*) and halfway between edge and seed (*2*), in the $+X$-zone near the edge (*4*) and near the seed (*5*) and in the $-X$-zone (*6*) in synthetic crystals. Numbers in parentheses refer to entries in tables 2 and 3 deposited with NAPS.

OH concentrations were also measured in the XY-plane along the X- and Y-axes in two samples of natural quartz from Brazil. The average distances between prism surfaces were 60 and 45 mm, respectively. Both samples were colorless and free from bubbles and cracks. The first was of almost perfect hexagonal shape, the second was somewhat distorted. They were sectioned perpendicular to the Z-axis and cut into pieces to fit into the cryostat.

III. Results and Discussion

Relative Intensities of Different Bands

Table I lists the OH vibration bands for synthetic quartz from the literature and from our study. The average relative intensities as a percentage of the total integral absorption for each of the bands are given also. The table also reflects the well-known fact that the OH spectrum of synthetic quartz more closely resembles that of natural amethyst than that of natural rock crystals. Some of the bands are termed characteristic for synthetic quartz because they are not found in natural clear quartz at all or as very weak features only. Examples are the bands at 3440, 3400, and 3355 cm^{-1}. The band at 3585 cm^{-1} may be termed the most characteristic of synthetic quartz, although it is relatively weak in comparison to other bands in the spectrum. Staats *et al.* (*12*) reported an additional band at 3595 cm^{-1} with H_3BO_3 as dopant in the

TABLE I

THE WAVENUMBERS OF INFRARED BANDS OF SYNTHETIC QUARTZ IN THE REGION 3200 cm^{-1} TO 3800 cm^{-1} AT 78°K

Wavenumbers (cm^{-1})				Intensities[a] as average of total absorption (%)	Notes
Dodd and Fraser (*3*)	Kats (*2*)	Kopp and Staats (*6*)	Present work		
	3615		3612	1	Present in amethyst (*2*)
	3600	3595	3595	2	Characteristic of synthetic quartz
3585	3585	3580	3585	5	Also present in amethyst (*2*)
	3565	3555	3565	4	Present in amethyst (*2*)
	3550		3550	5	
	3520	3515	3520	7	Present both in clear natural quartz and amethyst (*2*)
	3507	3500	3500	5	
	3480	3475	3480	10	
3440	3440	3438	3440	9	Characteristic of synthetic quartz and amethyst (*2*)
			3415	4	Present in clear natural quartz (*2*)
3400	3400	3396	3400	10	Characteristic of synthetic quartz and amethyst (*2*)
3370	3370	3368	3375	5	Present in clear natural quartz (*2*)
3365					
3355	3355	3350	3355	10	Characteristic of synthetic quartz and amethyst (*2*)
3311	3311	3300	3305	7	Very broad bands in comparison to others; Intensities are found to vary with the total integral absorption
	3280				
	3262				
	3240		3240	7	
	3222	3200	3205	9	

[a] Average of 23 results.

growth solution. In the present study a band at 3595 cm^{-1} was always observed, although no H_3BO_3 was present in the solvent. Kats (*2*) also reported a weak band at 3600 cm^{-1} in the case of synthetic quartz. The crystals he used were also grown without addition of H_3BO_3. This band at 3595 cm^{-1}, however, is not observable at room temperature.

Figures 2a to 2e show the relation between OH concentration associated with different bands and total OH concentration. The bands at 3585, 3520, 3440, 3400, and 3355 cm^{-1} increase linearly with total OH concentration, all the curves except Fig. 2c pass through the origin within the limits of error. We conclude that, in contrast to Fig. 1, there must be an additional band near 3440 cm^{-1} underlying the OH vibration spectrum. Within the limits of error this additional Si–O band does not contribute to the absorption bands at either 3400 or 3520 cm^{-1}, showing it to be of comparable or smaller halfwidth than the other Si–O bands. A curve with total integral absorption $K = 6$ cm^{2-} was included in Fig. 1 (dashed curve) and all absorption spectra were corrected for this extra absorption.

The Q-factors determined from the band at 3590 cm^{-1} at room temperature can be correlated with the total OH concentrations determined at 78°K.[2] An approximately inverse relationship holds between Q and total OH concentration. For higher OH concentrations a somewhat better fit is obtained with a relation of the type

$$1/Q = K_1 + K_2 \cdot [\mathrm{OH}] + K_3 \cdot [\mathrm{OH}]^2 \qquad [1]$$

where $K_1 = 0.5 \times 10^{-6}$, $K_2 = 5.8 \times 10^{-9}$, and $K_3 = 4.2 \times 10^{-12}$. Sawyer (8) used the same type of equation (with α_{3500} instead of OH/10^6 Si as in Eq. (1)). He obtained a negative value for K_3 for least-squares fitted results over a comparatively limited region of extinction coefficient (α_{3500}) values with $1/Q$ ranging up to 2×10^{-6} only. There is considerable scatter of the data points around the curve represented by Eq. (1). Perhaps a more precise determination of Q would be possible via infrared absorption measurements at 78°K rather than at room temperature. Our results clearly indicate that the intensity of any one of the bands in Fig. 2 and the total OH concentration could be used as an indication of the Q-factor of the crystal. Unfortunately, this does not give any hint as to which OH defects are actually responsible for the decrease in Q. If only synthetic quartz is considered, the total OH concentration may seem reasonable regardless of the different structures of defects associated with particular absorption bands. However, this conclusion is not supported by the experience with natural quartz crystals: OH concentrations in natural quartz are in some cases comparable to those of synthetic quartz, but the Q-factor of natural quartz is always found to be higher than in synthetic quartz, normally above 3×10^6 (*3*, *7*), whereas the highest Q-factor found in this series for synthetic quartz is 1.2×10^6. Despite a large variation of OH in different samples and in different parts of the same crystal, high and relatively constant Q-factors are characteristic for natural quartz. Evidently, OH defects prevailing in natural quartz have a rather low effect on mechanical Q while at least one of the OH centers characteristic for synthetic quartz has a strong effect. The most prominent bands in natural quartz occur at about 3370, 3305, and 3420 cm^{-1}; the typical bands in synthetic quartz are at higher energies. This suggests that OH groups not hydrogen-bonded to other oxygen ions of the lattice might be responsible for the decrease of Q. In addition, increasing proportions of more randomly oriented water molecules may make considerable contributions at higher OH concentrations, as indicated by band polarization measurements (*13*). This may be an explanation for the more than linear increase of $1/Q$ at higher OH concentrations.

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[2] Supplementary material regarding local variations of Q-factor and OH concentration in synthetic quartz has been deposited as Document No. NAPS 02796 with the National Auxiliary Publications Service, c/o Microfiche Publications, 440 Park Avenue South, New York, New York, 10016. A copy may be secured by citing the document number and by remitting $5.00 for photocopy or $3.00 for microfiche. Advance payment is required. Make check or money order payable to Microfiche Publications.

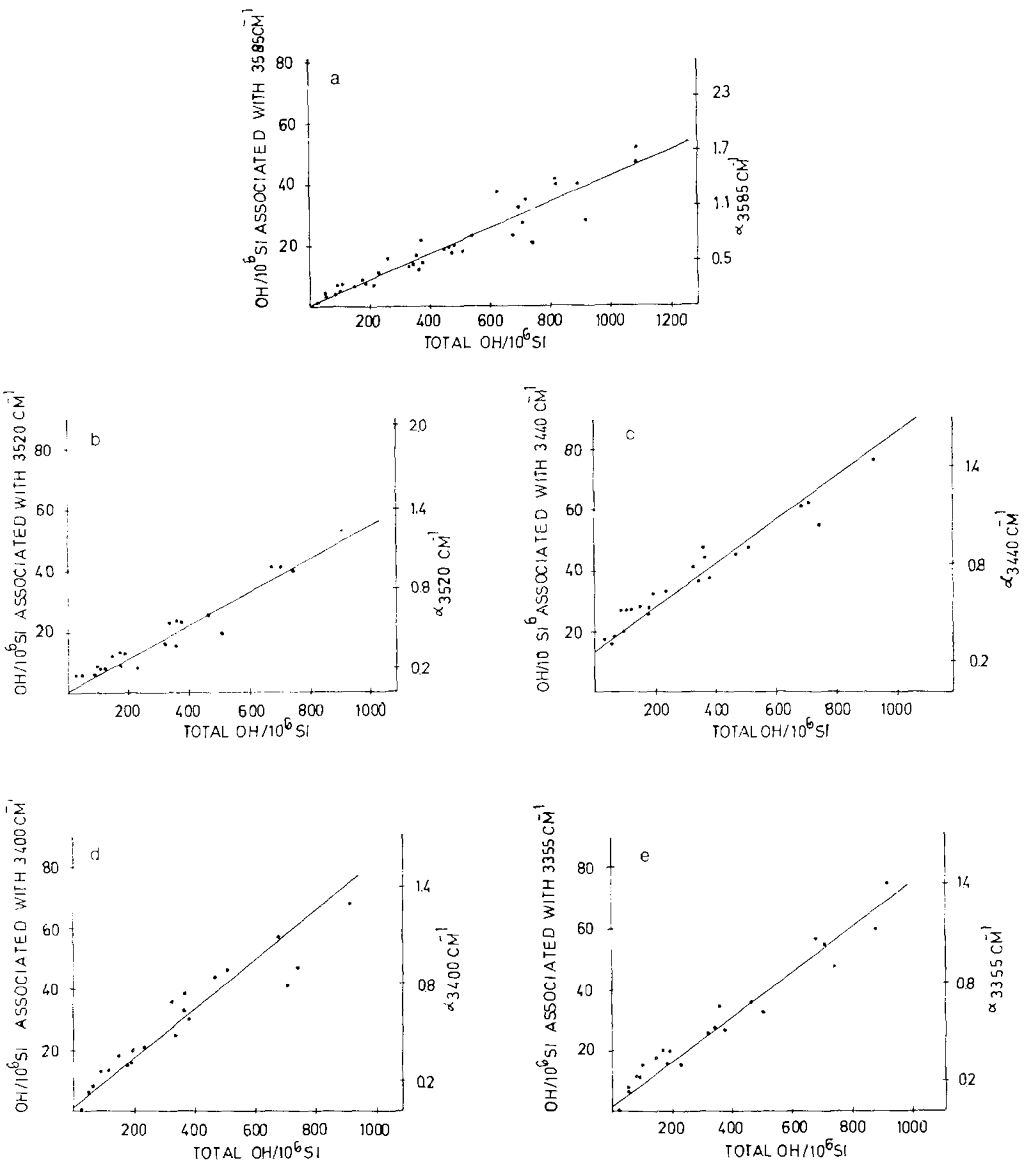

FIG. 2. Relation between OH concentration associated with a specific band and total OH concentration of the crystal. (a) 3585 cm^{-1} band; (b) 3520 cm^{-1} band; (c) 3440 cm^{-1} band; (d) 3400 cm^{-1} band; (e) 3355 cm^{-1} band.

Local Variation of OH Concentration

Results on the local variation of OH in synthetic quartz is expressed in terms of the *Q*-factor. As seen from the individual results and the average, the *Q*-factors calculated are highest for the *Z*-zone near the edge and lowest for the $-X$-zone with an overall four- to fivefold variation. Total OH concentration and the percentage associated with the band at 3585 cm^{-1} are listed. Here again, the lowest OH concentrations are present in the *Z*-zone near the edge. The relative concentration of the band at 3585 cm^{-1} does not vary significantly, either for different growth regions of the same crystal or for the more than thirtyfold variation in total OH concentration of differ-

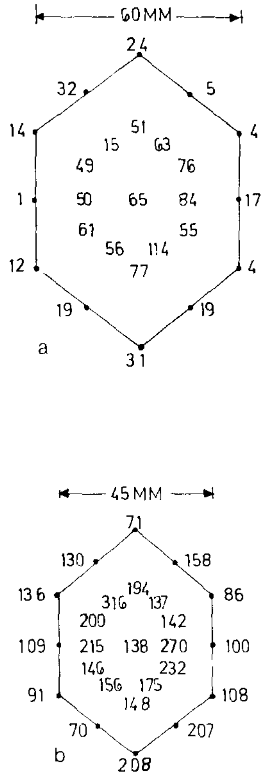

FIG. 3. Distribution of OH in two clear natural quartz crystals along *X*- and *Y*-axes in the *XY*-plane. The numbers represent OH/10^6 Si.

ent crystals. (The seemingly higher ratio for small OH concentrations easily may be due to small errors in baseline location.) The local variation of OH closely resembles the variations of metal impurity contents in different growth regions (*14*), suggesting that there is a relatively constant proportion of charge compensation for lower valence impurities, noticeably Al^{3+}, by OH groups.

For natural quartz, the sum of the alkali and hydrogen contents approximately equals the Al concentration (*4*), also suggesting charge compensation by either alkali or hydrogen. For Fe^{3+} in amethyst, these types of charge compensation are evident from the EPR spectra of Fe^{3+} in Si sites (*15, 16*).

Figures 3a and 3b demonstrate the local variations of OH in the two natural quartz crystals from Brazil. OH concentrations near the edge are lower than in other parts, similar to synthetic quartz. We did not determine the sign of X directions for these samples, but if we assign the edges with the highest OH content (lower corners in Fig. 3) as one of the $-X$ directions, we get ratios of 1.6 in Fig. 3b and 1.22 in Fig. 3a respectively, for the ratios of the sum of OH concentrations in the negative and positive X directions. However, these ratios change to 1.08 and 0.86, respectively, for the inner parts of the crystals. Thus, the differences for the positive and negative X directions in natural quartz cannot be nearly as large as those in synthetic crystals.

IV. Conclusions

The integral absorptions of OH bands associated with various defects in synthetic quartz samples were found to vary linearly with total OH concentration over the whole range of OH concentrations studied. Consequently, mechanical Q of synthetic quartz could be related with any one of these bands as well as with the total OH concentration. However, using a relation between Q and the extinction coefficient at 3590 cm^{-1} at room temperature given in the literature (*7*), correlation of Q determined in this way with total OH concentration determined at 78°K leads to a rather large scatter of data. Further work must show whether absorption measurements at 78°K are a more precise method of indirect determination of Q. Since natural quartz is known to have higher and relatively constant Q values despite the comparable and largely variable contents of OH, one or all of the OH defects characteristic for synthetic quartz must have a rather high effect on mechanical Q, whereas the effect of all OH defects characteristic of natural quartz must be small. At present, we are investigating polarization ratios for the various OH absorption bands to establish models for the defects associated with them.

OH concentrations in different growth zones vary in the order $Z < +X \ll -X$, the same as found for impurity concentrations in synthetic quartz. This strongly suggests that OH acts as a charge compensator for metal impurities like Al^{3+}. Since the growth rate is smallest for $-X$

and highest for *Z*, different degrees of adsorption of these impurity ions or of OH may be responsible for the observed variations of both relative growth rates and impurity uptake in different growth regions.

Similar to synthetic quartz, OH concentrations of natural quartz along the *X*- and *Y*-axes are lower near the edge than in interior parts of the crystals. However, the differences for different directions are not nearly so large as in synthetic quartz.

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