# RELATIONSHIPS AMONG IMPURITY CONTENTS, COLOR CENTERS AND LATTICE CONSTANTS IN QUARTZ

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## Abstract

The lattice constants of four specimens of synthetic and seven of natural quartz have been measured. The $a_0$ axis appears the more sensitive to impurity content.

## Introduction

That a color center in $\alpha$-quartz is impurity related is now well established (1). This anisotropic color center at 460 $m\mu$ (2, 3) is caused by the interaction of an unpaired electron on an oxygen (or possibly in an anion vacancy) with an aluminum ion replacing a tetrahedral silicon in the quartz structure (4).

Although several other color centers have been reported in quartz, none of these has been specifically related to a given impurity in the quartz (5). Frondel and Hurlbut (6) state that unit cell size increases with increasing substitution of aluminum for silicon in the structure and that smoky quartz has smaller cell dimensions than colorless, the content of trace elements of the two samples being about the same. This contradiction will be explained later. Wittels (7) has subjected $\alpha$-quartz with lattice constants $a_0 = 4.903$ Å and $c_0 = 5.393$ Å to $6.6 \times 10^{19}$ *nvt* of total integrated neutron flux. The lattice constants were expanded to $a_0 = 5.01 \pm 0.01$ Å and $c_0 = 5.41 \pm 0.02$ Å. The increase in lattice size thus was due within experimental error entirely to anisotropic expansion in the $a$ direction. According to Wittels the most probable positions for dislocated atoms are the interstitial spaces which form long channels parallel to the $c$ axis; and the stuffing of these voids would account for the expansion in the $a$ direction.

Keith and Tuttle (8) have studied the effect of impurities on the inversion temperature of quartz and find that aluminum and lithium tend to be more soluble in the $\beta$ phase and lower the inversion temperature while the results found for germanium are the opposite.

H. D. Keith (9) in a recent note on the variability of the quartz lattice suggests that impurity atoms or ions would have a larger effect in the plane normal to the optic axis than in the direction parallel to it due to the channels paralleling the latter direction. He suggests that impurities normally found in quartz whether interstitial or substitutional,

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tend to increase the lattice spacings as the radius of $Si^{+4}$ ion is smaller than that of any other ion likely to replace it.

Sabatier and Wyart (10) on the contrary, find that the $a_0$ parameter is smaller in synthetic quartz to which sodium has been added. They state that the $c_0$ is unchanged and the transition temperature is raised. These findings conflict with those of the present paper.

Hammond and coworkers (11) have studied the form and width of diffraction lines of synthetic quartz containing controlled impurities. Their method is capable of an accuracy of two parts in $10^7$. They find that the defects responsible for blackening smoky quartz (now known to be aluminum) move toward the negative electrode on heating quartz to 530° C. in the presence of a field of 3000 v. across a thickness of 6 mm. Reirradiation indicates that the impurity moves along the Z direction of the crystal. In the region cleared by the field the lattice spacing is decreased toward that associated with a nearly perfect crystal. They find the lattice spacing to expand with increasing concentration of impurities. Their results thus indicate that substitutional aluminum can be moved in quartz under the influence of an electric field.

## EXPERIMENTAL

The samples were prepared for the $x$-ray powder diffraction work by grinding to 325 mesh and loading into 0.3 mm. internal diameter, thin-walled capillary tubes. A Buerger-type, Debye-Scherrer camera of 11.46 cm. diameter with 1.0 mm. pinholes was used to obtain the diffraction patterns. Twenty-four hour exposures to CuK$\alpha$ radiation (using a nickel filter only) were made at $25 \pm 1°$ C. The positions of the diffraction lines used were read to the nearest 0.02 mm. using the film measuring device described by Klug and Alexander (12). The effective film circumference was then obtained from these line positions after the method of Strau-manis. The cell dimensions were determined by the graphical method of successive approximations (13) using an initially assumed axial ratio $(c/a)$ of 1.10004 (14) and the wide-angle extrapolation function of Taylor and Sinclair (15), viz.

$$f(\theta) = 1/2 \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right).$$

Occasionally three extrapolations were required before consistency of the lattice constants was obtained. In general, however two extrapolations were found to be sufficient. The lattice constant determinations for each quartz sample were made with the following diffraction lines, the angular range of which extends from 59.1 to 79.3° $\theta$: CuK$_{\alpha 1}$ lines ($\lambda = 1.53740$ kX or 1.54040 Å (16)) for $hkl$ values of 126, 135, 240, 330, 206, 501, 116, 142, 106, and 125; and CuK$_{\alpha 2}$ lines ($\lambda = 1.54124$ kX or

TABLE 1. IMPURITY CONTENTS OF NATURAL AND SYNTHETIC QUARTZ AS DETERMINED BY EMISSION ANALYSES

| Impurity | Brush Synthetic[1] % [7] | Bell Synthetic (R-31)[2] % [7] | Dinkey Lakes, Cal. Smoky[3] % [7] | Bell Synthetic (R-537)[2] % [7] | Bell Synthetic (R-27)[2] % [7] | Brazilian Amethyst[4] % [7] | "Greened" Amethyst[4] % [7] | Volcanic[5] % [7] | Rose[6] % [7] | Topaz[6] % [7] |
|---|---|---|---|---|---|---|---|---|---|---|
| Ag | 0.0001 | 0.0001 | N.F. | 0.001 | 0.0001 | 0.0001 | <0.0005 | 0.0001 | 0.0001 | 0.0001 |
| Al | 0.003 | 0.003 | 0.01 | 0.01 | 0.03 | >0.01 | 0.005 | >0.01 | >>0.01 | ~0.01 |
| Bi | N.F. | N.F. | N.F. | 0.001(?) | N.F. | N.F. | N.F. | N.F. | N.F. | N.F. |
| Ca | 0.0003 | ~0.001 | 0.003 | ~0.001 | ~0.001 | 0.003 | >0.0005 | ~0.01 | 0.003 | 0.003 |
| Cr | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.001 | N.F. | <0.002 | 0.003 | N.F. | N.F. |
| Cu | 0.001 | 0.001 | 0.01 | 0.003 | 0.003 | >0.0001 | <0.0005 | ~0.0001 | ~0.0001 | <0.0001 |
| Fe | 0.003 | ~0.001 | 0.001 | ~0.001 | 0.01 | ~0.01 | >0.005 | ~0.01 | >0.01 | >0.01 |
| Ge | N.F. | 0.01 | N.F. | N.F. | 0.1 | N.F. | N.F. | N.F. | N.F. | N.F. |
| K | N.F. | N.F. | N.F. | N.F. | N.F. | N.S. | N.S. | N.S. | N.S. | N.S. |
| Li | 0.0003 | 0.0001 | 0.0003 | 0.0003 | 0.01 | N.S. | N.S. | N.S. | N.S. | N.S. |
| Mg | <0.001 | <0.001 | ~0.003 | <0.001 | <0.003 | ~0.001 | <0.0005 | ~0.01 | ~0.001 | ~0.001 |
| Mn | N.F. | N.F. | 0.003 | 0.003 | N.F. | N.F. | N.S. | N.F. | N.F. | N.F. |
| Na | 0.003 | 0.003 | 0.003 | N.F. | 0.003 | N.F. | N.S. | N.S. | N.S. | N.S. |
| Ni | N.F. | N.F. | N.F. | N.F. | N.F. | N.F. | 0.001 | ~0.001 | N.F. | N.F. |
| Pb | N.F. | N.F. | N.F. | 0.003 | N.F. | N.F. | <0.05 | 0.003 | N.F. | N.F. |
| Rb | N.F. | N.F. | N.F. | 0.03 | N.F. | N.S. | N.S. | N.S. | N.S. | N.S. |
| Ti | N.F. | N.F. | N.F. | N.F. | N.F. | trace (?) | N.F. | 0.003 | 0.003 | trace (?) |

[1] Specimen courtesy Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.
[2] Specimen courtesy Dr. G. T. Kohman, Bell Telephone Laboratories, Murray Hill, New Jersey.
[3] Specimen courtesy Dr. Ronald A. Henry, China Lake, California.
[4] Specimen courtesy Eldot and Company, New York 23, New York. Contains 0.001% Zr in addition to above.
[5] Specimen collected by senior author from pack rat's nest in rock shelter near Little Lake, California. Contains ~0.001% Sn in addition to above.
[6] Specimen courtesy Inter-Ocean Trade Company, New York 36, New York.
[7] Absolute value believed to be between $\frac{1}{3}$ and 3 times the value indicated.
N.F. = not found.
N.S. = not sought.

1.54434 Å) for *hkl* values of 126, 241, 240, 331, 330, 206, 501, 116, 142 and 125. The forms of the Bragg equation used for the calculation of the hexagonal cell dimensions are

$$a_0 = \frac{\lambda}{2 \sin \theta} \sqrt{\frac{4}{3} S + (a/c)^2 l^2} \quad \text{and} \quad c_0 = \frac{\lambda}{2 \sin \theta} \sqrt{\frac{4}{3} (c/a)^2 S + l^2},$$

where $S = h^2 + hk + l^2$.

The samples were prepared for emission analysis by grinding in a boron carbide mortar used exclusively for grinding high purity silica samples.

## RESULTS AND DISCUSSION

Table I lists the impurity contents of four specimens of synthetic quartz, a smoky quartz, an amethyst, an amethyst which remains green after heat bleaching (5), a quartz of volcanic origin, a rose quartz and a topaz colored quartz. Emission analyses for alkali content were made for only the first five of the listed specimens. Results presented in this table will be discussed in conjunction with the lattice constants determined for these materials.

Table II lists the lattice constants both in kX units and in angstrom units in order to make comparison with other work easier. The lattice constants of a colorless Herkimer, N. Y., quartz are reported for which no impurity content datum is available. This crystal was about a mm³. in volume and there was not enough material available for emission

TABLE II. LATTICE CONSTANTS OF NATURAL AND SYNTHETIC
QUARTZ AT $25 \pm 1°$ C.

| Quartz | $a_0$(kX)[1] | $c_0$(kX)[1] | $a_0$ (Å)[2] | $c_0$ (Å)[2] | $c/a$[3] | $d$ calc. |
|---|---|---|---|---|---|---|
| Brush Synthetic | 4.9035[4] | 5.3940[4] | 4.9134 | 5.4049 | 1.10003 | 2.6489 |
| Bell Synthetic (R-31) | 4.9034 | 5.3942 | 4.9133 | 5.4051 | 1.10009 | 2.6489 |
| Dinkey Lakes, Smoky | 4.9033 | 5.3941 | 4.9132 | 5.4050 | 1.10011 | 2.6489 |
| Bell Synthetic (R-537) | 4.9033 | 5.3943 | 4.9132 | 5.4052 | 1.10014 | 2.6489 |
| Bell Synthetic (R-27) | 4.9040 | 5.3943 | 4.9139 | 5.4052 | 1.09997 | 2.6483 |
| Amethyst, Brazil | 4.9035 | 5.3938 | 4.9134 | 5.4047 | 1.09999 | 2.6489 |
| Amethyst, "Greened" | 4.9032 | 5.3938 | 4.9131 | 5.4047 | 1.10006 | 2.6493 |
| Herkimer, Colorless | 4.9035[4] | 5.3941[4] | 4.9134 | 5.4050 | 1.10005 | 2.6487 |
| Volcanic | 4.9039 | 5.3938 | 4.9138 | 5.4047 | 1.09990 | 2.6485 |
| Rose | 4.9042 | 5.3943 | 4.9141 | 5.4052 | 1.09993 | 2.6481 |
| Topaz | 4.9032[4] | 5.3942[4] | 4.9131 | 5.4051 | 1.10014 | 2.6491 |

[1] Error $\pm 0.0002$ kX.

[2] kX $\times 1.00202$ to give Å.

[3] Calculated from kX values.

[4] Average of measurements by two persons, each of which was within the experimental error.

analysis. This small crystal was discovered on the face of a larger crystal which turned smoky on continued x-ray treatment while the smaller crystal developed no visible coloration even after a dosage of many millions of röntgens. This suggests that no aluminum is present substitutionally, as no visible color center giving a resulting smoky color is present. Its measured cell dimensions $a_0 = 4.9035$ kX and $c_0 = 5.3941$ kX both $\pm 0.0002$ kX match the measurements of Frondel and Hurlbut (6) for colorless Herkimer quartz within the experimental errors, their values being $a_0 = 4.9031$ and $c_0 = 5.3938$ kX both $\pm 0.0003$ kX. Comparing these values to the other lattice constants in Table II, one may conclude that the Herkimer quartz contains interstitial impurity (based on expansion of $a$ axis) and substitutional impurity other than aluminum (based on expansion of $c$ axis). This statement will become clearer as the discussion continues. Keith (14), for example, has reported cell dimensions $a_0 = 4.90309$ kX and $c_0 = 5.39367$ kX (25°) for a Brazilian quartz which presumably has a low impurity content. He claims an accuracy of 1 part in $10^5$ for this measurement.

Keith (14, 9) has pointed out that the axial ratio, $c/a$, decreases as the parameters increase. He states that the elastic anisotropy of quartz suggests that if impurities are present and cause a small *stress* in the lattice which is homogeneous, then this behavior of the axial ratio can be explained. He derives values for the "increment ratio"

$$\left( \frac{\Delta a}{a} \Big/ \frac{\Delta c}{c} \right)$$

for four specimens and finds a mean value of 1.39. This value is then compared to the ratio of adiabatic values of the strain components $S_{11}(1.269 \times 10^{-12})$ parallel to the optic axis and $S_{33}(0.971 \times 10^{-12})$ normal to the optic axis, which is 1.307. Keith then concludes that this agreement indicates that an impurity content in quartz produces a small stress in the lattice and consequent alterations in the parameters. Thus he states that the effect of impurities should be greater in the plane normal to the optic axis than in the plane of the optic axis. A comparison of the cell dimensions reported in the present work are made using Keith's "increment ratio." However, Keith's procedure for obtaining his "increment ratios" by exhaustive cross-comparison was was not employed since it is inappropriate for samples of our series containing interstitial impurities. Instead, the values of Keith's (9) Brazilian quartz are chosen for comparison purposes as being low in impurity content. Nevertheless, some impurity must be present in this sample since Frondel and Hurlbut (6) report $a_0 = 4.90299$ kX and $c_0 = 5.39353$ kX ($\pm 0.0001$ kX) for a smoky quartz. Table III gives calculations of the ratio

$$\left(\frac{\Delta a}{a}\bigg/\frac{\Delta c}{c}\right)$$

using $a_0 = 4.90309$ kX and $c_0 = 5.39367$ kX ($25°$ C.) as the standard for comparison. The data of this investigation is tabulated with the decrease in $c/a$ ratio. It is seen that the "increment ratio" increases regularly as the $c/a$ ratio decreases with only two exceptions, the Brazilian amethyst

TABLE III

| Specimen | "Increment Ratio" $\left(\dfrac{\Delta a}{a}\bigg/\dfrac{\Delta c}{c}\right)$ | $c/a$ |
|---|---|---|
| Topaz Quartz | 0.220 | 1.10014 |
| Bell Synthetic (R-537) | 0.367 | 1.10014 |
| Dinkey Lakes (Smoky) | 0.550 | 1.10011 |
| Bell Synthetic (R-31) | 0.660 | 1.10009 |
| "Greened" Amethyst | 1.100 | 1.10006 |
| Herkimer, New York | 1.100 | 1.10005 |
| Brush Synthetic | 1.467 | 1.10003 |
| Brazilian Amethyst | 4.400 | 1.09999 |
| Bell Synthetic (R-27) | 1.650 | 1.09997 |
| Rose Quartz | 2.017 | 1.09993 |
| Volcanic Quartz | 8.801 | 1.09990 |
| Herkimer, New York[1] | 0.110 | 1.10008 |
| Carrara, Italy, Colorless[1] | 0.667 | 1.10008 |
| Synthetic ($890°$)[1] | 1.015 | 1.10006 |
| Smoky (101)[1] | 0.785 | 1.10005 |
| Rose (111)[1] | 1.086 | 1.10004 |
| Colorless (105)[1] | 1.122 | 1.10004 |
| Rose (102)[1] | 1.358 | 1.10004 |
| Synthetic $800°$ (Na $WO_3$ melt)[1] | 1.466 | 1.10003 |
| Synthetic $600°$ (Al+Li)[1] | 1.344 | 1.10000 |

[1] Calculated from work of Frondel and Hurlbut, Reference 6.

and the volcanic quartz. Figure 1 is a plot of $c/a$ vs. the "increment ratio" for the data of Table III. The points for the work from this laboratory fall along a straight line except for the above two samples.

The distribution of the impurities in the samples of Table III will now be discussed individually. The assignment of impurity to substitutional or interstitial sites will rest mainly on the argument that interstitial impurities should expand only the $a$ directions markedly. Work now in progress in this laboratory is aimed at a more direct demonstration of this plausible assumption.*

* Cohen, A. J., Substitutional and Interstitial Aluminum Impurity in Quartz, Structure and Color Center Interrelationships: Symposium on the Defect Structure of Quartz and Glassy Silica, Mellon Institute, May 1957.

The deviation of two quartzes from the straight line in Fig. 1 is most likely due to the predominance of interstitial impurities over substitutional as shown by the greater relative increase in the $a$ dimension. The fact that color centers characteristic of substitutional aluminum are not present in amethyst (5) is most likely due to the fact that the aluminum impurity in this quartz is mainly interstitial and not in the proper environment for color center formation.

The quartzes that have a large percentage of their aluminum in substitutional positions as evidenced by the fact that the color center at 460 m$\mu$ correlates with the aluminum content (3) are the four synthetic and
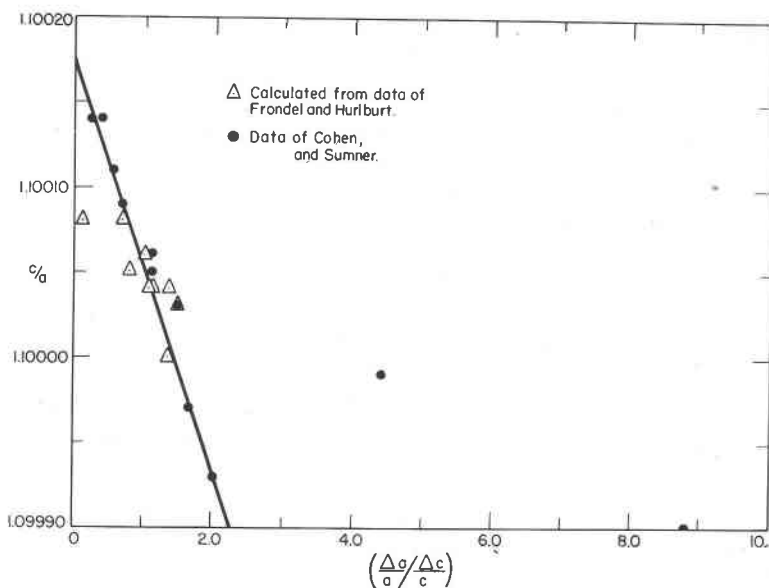


FIG. 1. Plot of "increment ratios" versus axial ratios of $\alpha$-quartzes.

the Dinkey Lakes Smoky. In the ones having Al content between 0.003 and 0.01 per cent by weight, the "increment ratio" varies from 0.367 to 1.467 and the $c/a$ ratio between 1.10014 and 1.1003. The Bell Synthetic (R-27) with "increment ratio" of 1.650 and $c/a$ of 1.09997 has an aluminum impurity content of 0.03 per cent and is higher in germanium and lithium impurity than Bell Synthetic (R-31). One concludes that both the substitutional and interstitial impurity contents of this specimen are high.

The rose quartz of this laboratory's series turns smoky upon $x$-irradiation so a portion of its aluminum content at least is substitutional. It

contains rutile as a separate phase, as do all other rose quartz specimens that were examined under the microscope in this laboratory. The "increment ratio" of 2.017 and $c/a$ of 1.09993 indicate the expansion in the $a$-direction, the $a_0$ being 4.9042 kX which in turn indicates a high content of interstitial impurities. On the other extreme is the topaz quartz from Rio Grande, Brazil with "increment ratio" of 0.220 and $c/a$ of 1.10014; it has the lowest $a_0$ reported in this paper, 4.9032 kX, along with a $c_0$ of 4.3942 kX, rather on the high side. This would indicate that the impurity content, largely aluminum and iron, is present substitutionally.

The volcanic quartz with high impurity content and a $c_0$ on the low side seems definitely to have mainly interstitial impurities as mentioned earlier. The "greened" amethyst with $a_0 = 4.9032$ kX must be low in interstitial impurities compared to its substitutional impurity content. This specimen exhibits the laminar $d$-,$l$-twining associated with amethyst with a separate phase responsible for the green color. This separate phase probably accounts for some of the aluminum, iron and magnesium impurity present. The amethyst discussed earlier with the suggestion that the impurity content was largely interstitial did not exhibit as pronounced laminar twinning as found in the "greened" amethyst.

The calculations of "increment ratios" made on data of Frondel and Hurlbut indicate that their Herkimer quartz is higher in substitutional impurities as is the colorless quartz from Carrara, Italy. The Synthetic 800° ($NaWO_3$ melt), Synthetic 600° ($Al+Li$) and Rose (102) seem higher in interstitial impurities than the others. In using their lattice constants the same general trend continues with the "increment ratio" increasing with decreasing $c/a$. As shown in Fig. 1 the plot of "increment ratio" vs. $c/a$ agrees well with data from this laboratory except for the Smoky (101). The cell dimensions of this quartz are smaller than those chosen for comparison purposes. The values given (6) are $a_0 = 4.90299$ and $c_0 = 5.39353$ kX both $\pm 0.0001$ kX. It is on the basis of this result that Frondel and Hurlbut make the statement that smoky quartz has smaller unit cell dimensions than colorless quartz of the same impurity content. An explanation for this finding in view of results presented here is that most of the impurity content of this particular smoky quartz is substitutional. The aluminum must be thus, in order for a smoky color to be produced. The colorless varieties might contain more of their impurity content as interstitials which would cause a greater expansion of the $a$-axis than of the $c$-axis and possibly a greater expansion of the $a$-axis than caused by the same amount of the same substitutional impurity. To compare a smoky quartz to a colorless one properly, the quartz should be $x$-irradiated to determine whether a smoky color can be de-

veloped. Then a colorless region may be compared to a colored region such as actually exists in Y-bar synthetic quartz produced by the Clevite Research Center as shown by work of J. M. Jost (17). No investigation has been made of the effects of color center formation on lattice dimensions; this would presumably lend a smaller effect than that of the impurity content. Hammond *et al.* do mention a small but significant change in the width of the $(12\bar{3}1)$ reflection before and after heat bleaching of a smoky quartz (11).

The color center phenomena in the 320–1000 m$\mu$ region has been discussed earlier (3) in detail for the Brush Synthetic, the three Bell Synthetic and the Dinkey Lakes, California quartzes. They all exhibit two anisotropic color centers with maxima at 460 and about 625 m$\mu$ related to aluminum present in a substitutional position. These specimens exhibit a relationship between the amount of aluminum found by emission spectral analysis and the saturation absorption coefficient of the color centers that are dependent on substitutional aluminum impurity. Therefore in these synthetic quartzes grown from AT or BT cut seed plates and in the natural smoky quartz studied here the aluminum impurity is mainly substitutional. This may not be the case for all quartz. For example Arnold (18) and Jost (17) find that there is poor agreement in some instances. This is evidence for interstitial aluminum being present in these samples. Work in progress in this laboratory on synthetic quartz (Sample No. 515B) grown on a Z cut seed at General Electric Co. Ltd. (Wembley, England) shows 130 *p.p.m.* of aluminum present although no color centers were developed in the visible region even after $3.8 \times 10^8 r$ of x-ray dosage (in air at surface of sample). This indicates that aluminum can occupy an interstitial position as well as a substitutional position in the quartz structure.

The color centers in the "greened" amethyst have been discussed earlier (5).

## Conclusions

By comparing "increment ratio," axial ratio, lattice constants, impurity analysis and color center formation, one may generalize concerning the impurity positions in the quartz structure. Cationic impurities in quartz may be substitutional replacing $Si^{+4}$, or interstitial. In order to preserve electroneutrality *e.g.* one interstitial $Li^+$ per substitutional $Al^{+3}$, or one interstitial $Al^{+3}$ per three substitutional $Al^{+3}$ ions could be present provided balance is not achieved through oxygen vacancies. In addition quartz containing only interstitial aluminum, as is the case with the G. E. synthetic quartz mentioned, has its interstitial $Al^{+3}$ accompanied by an equivalent amount of interstitial $Li^+$ (emission analysis gives 290 Al and 260 Li per $10^6$ Si atoms). Another source of impurity

that confuses chemical and emission analyses of quartz is that present as a separate microscopic phase as in rose quartz or as a submicroscopic phase as in the laminar twined variety of quartz.

Since interstitial impurities mainly cause expansion of the *a* axis and substitutional impurities cause expansion of both axes, the following generalizations may be used to gain information concerning impurities present where "increment ratio" and axial ratio correlate (as for seventeen of twenty cases in Fig. 1):

(1) a low "increment ratio" ($\sim$1.5 or less) indicates the $\alpha$-quartz contains mainly substitutional impurities and these impurities have radii larger than $Si^{+4}$.

(2) an intermediate "increment ratio" ($\sim$1.4–1.7) indicates both substitutional and interstitial impurities are present.

(3) a high "increment ratio" ($>$1.7) or lack of correlation between this and axial ratio indicates that a high percentage of the impurity is interstitial.

## ACKNOWLEDGMENTS

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