JOURNAL OF SOLID STATE CHEMISTRY **109**, 106–111 (1994)

A New Approach of the –OH Content in Berlinite Crystals

J. M. Durand, A. Ibanez, A. Goiffon, and E. Philippot[1]

Laboratoire de Physicochimie des Matériaux Solides, URA CNRS D0407, case 003 UMII, Place E. Bataillon,
F-34095 Montpellier Cedex 5, France

Received January 21, 1993; in revised form June 21, 1993; accepted July 1, 1993

In view of the numerous methods, often inconsistent, proposed to quantify the OH content from IR measurements in the piezoelectric materials as quartz and MXO_4 (M = Al, Ga and X = P, As) quartz-like crystals, we have reinvestigated this determination. This knowledge is very important, because it is closely related to piezoelectric properties, in particular the Q factor, which is drastically reduced by this impurity. After a brief overview of previous studies devoted to quartz and berlinite crystals, we develop a formula taking into consideration an anisotropic factor, γ, for the OH content distribution. This relation has been applied to IR measurements of a berlinite bar. Then, the C_{OH} content can be directly estimated from the height, K, of the 3300 cm^{-1} absorption band: $C_{OH/(Al+P)}$ ppm = 907 K with an isotropic OH distribution. © 1994 Academic Press, Inc.

INTRODUCTION

Infrared spectroscopy has long been used to characterize water molecules and hydroxyl groups bound to cations in ores (1–9). To prevent drastically decreasing piezoelectric properties of materials like α-quartz and berlinite, AlPO4, the OH content must be minimized (10–14). Understanding this problem involves accurately determining their OH content and explaining how their mode of incorporation influences physical properties.

For α-quartz crystals, a careful study was first developed by Kats (15) for hydrogen atom incorporation and, subsequently, much work has been devoted to answering questions pertaining to qualitative and quantitative purposes (16–23). Another consequence of this OH content is its role in material distortion under constraints (24–26). In view of the strong similarities between properties and behavior of α-quartz and berlinite crystals, results for α-quartz have been extended to berlinite (14, 27–29).

These previous studies have demonstrated the importance of the OH defects for piezoelectric applications of α-quartz and berlinite materials. Results obtained from infrared spectrometry are strongly related to many factors: sample orientation, beam polarization and orientation, surface state, temperature, etc. All these parameters are not always specified and make difficult any comparison between results. On the other hand, many equations are proposed to quantify the OH content, but some ambiguities exist as regards their application.

Within the framework of our work involving the compounds, $M^{III}X^{V}O_4$ (M = Al, Ga, Fe; X = P, As) quartz-like materials, we have first developed growth conditions and quality determinations of berlinite crystals (14). For the OH content, a relation has been proposed to give a semiquantitative idea of this amount (12). Thus, one can follow the OH content evolution in terms of crystal growth parameters and, then, its influence on physical properties. Unfortunately, this relation does not give an absolute value of the OH content. Thus, relying on previous work devoted to α-quartz, we have tried to quantify the OH groups for berlinite crystals, taking into account their orientation. Before developing our results, we recall the main relations previously established.

I. RECALL OF PREVIOUS RELATIONS

Table 1 summarizes the different formula proposed to quantify the OH and H_2O content in α-quartz and berlinite crystals. These two major hydrogen species, H_2O and OH, can be easily differentiated using near infrared, NIR. Indeed, molecular water shows an absorption near 5200 cm^{-1} due to combination mode [stretching (Wavenumber: 3500 cm^{-1}) + bending (1650 cm^{-1}) modes] which is missing for the hydroxyl groups. On the other hand, these OH groups absorb nearly 4500 cm^{-1} due to another combination mode [(stretching (3500 cm^{-1}) + bending Al–O–H (950 cm^{-1}) modes] (5, 22).

In these different proposed relations, we can note some important differences:

—Sometimes, the entire stretching absorption band is integrated, whereas in other cases only its height is measured.

—The ε value changes from one study to another.

—The anisotropic factor, γ, which depends on the OH distribution, is never taken into account.

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[1] To whom correspondence should be addressed.

0022-4596/94 $6.00

TABLE 1
Different Formulas Proposed to Quantify the –OH Content in Quartz and Berlinite Crystals

No.	Formula	Units	Observations	References
		α-Quartz (SiO_2)		
1	$C = \int \frac{K(\nu)d\nu}{150\gamma(3780-\nu)} = \frac{\Delta}{I}$	H liter^{-1}	k : maximum absorption coefficient ν : wavenumber γ : anisotropy factor I : Integral molar absorption coefficient	(21)
2	$C = 1.05\,\Delta_{\mathrm{cm}^{-2}}$	OH/Si ppm	Δ : Integral absorbance from 3750 to 2400 cm^{-1} polarized $E \perp c$	(22)
3	$C = A^{a}\,45.35/\varepsilon$	OH/Si ppm	NIR ε : molar extinction coefficient for H_2O $E \parallel c$	(22)
4	$C = A/\varepsilon\, d^{a}$	mole (H_2O) liter^{-1}	Molecular water in fluid inclusions 3400 cm^{-1} ε = 81 liter mole^{-1} cm^{-1}	(5)
5	$C = \int \frac{Af}{d\varepsilon} d\nu = 2.11\,K$	OH/Si ppm	Unpolarized light $K = \int E d\nu / d$ = integral absorption $f = 10^6 \rho / M$ (ρ = quartz density and M = molar weight)	(17)
6	$N = 2.16 \times 10^{16}\,K$ $C = 0.81\,K$	OH cm^{-3} OH/Si ppm	Unpolarized light incident $\perp$, c-axis K = OH αm with αm = absorption coefficient at the peak and H = corresponding halfwidth	(15)
7	$C = \frac{2}{3} \frac{\Delta(cm^{-2})}{14000}$	OH liter^{-1}	Unpolarized $\parallel$ to the c-axis	(31)
8	$\alpha = \frac{1}{d} \log \left\{ \frac{(1-R)^2}{2T} + \left[\left(\frac{(1-R)^2}{2T} \right)^2 + R^2 \right]^{1/2} \right\}$		T = transmission R = reflectivity Unpolarized beam	(23)
9	$\alpha = \frac{A_{3500} - A_{3800}}{d}$			(10)
10	$c = 88\,\alpha_{3500}$	Berlinite ($AlPO_4$) H_2O ppm by weight	Used for SiO_2 or $AlPO_4$ ε = 77.5 liter mole^{-1} cm^{-1}	(30)
11	$H_2O(ppm) = 18{,}000/\varepsilon\rho d \log I_0/I$ or $H_2O(ppm) = 48.73/d \log(I_0/I)$ $= 48.73\,\alpha$		ε = molar extinction coefficient = 141 liter mole^{-1} cm^{-1} formula derived from one suggested to measure the water content of B_2O_3 $\alpha = 1/d \log I_0/I$	(13)
12	$H_2O(ppm) = 48.73\,\alpha$ $\alpha = 1/d \log(T_{3800}/T_{3300})$		$\alpha = 1/d \log T_{3800}/T_{3300}$ definition of α different between 11 and 12 T_{3800} and T_{3300} = relative background transmission and peak absorption	(12)
13	$C = \frac{1.07}{d} \int_{2500}^{4000} \log \frac{T(\nu)}{I(\nu)} d\nu$	H/(Al + P) atom. ppm $C_{H/(Al+P)ppm} \cdot 14.8 \times 10^{-2} = C_{H_2O/AlPO_4}$ weight	$T(\nu)$ and $I(\nu)$ = transmitted and incident intensities at the wave number ν	(28)

[a] A = absorbance, d = sample thickness (cm).

In view of these differences, we have undertaken to propose a new method to quantify the OH content in berlinite crystals, taking all these previous remarks into account.

II. PROPOSED FORMULA TO QUANTIFY THE OH CONTENT IN BERLINITE BY IR SPECTROMETRY

Among the different methods already used, it seems that the Paterson method (21) is the most suitable. In fact, the same calibration can be used for a wide range of compounds such as silicate glasses, quartz, and similar materials. In this case, the distribution of OH orientation is taken into account. The OH content can be estimated with the maximum incertitude lower than 40%, which is not a high value in comparison with the other methods. Berlinite being a quartz-like material, this relation can give a good approximation of the OH content related to wide band absorption of berlinite crystals at 3300 cm^{-1}.

Using this calibration,

$$I_{\parallel} = I/\gamma = 150(3780 - 3300) = 72{,}000\,\mathrm{cm}^{-1}, \qquad [1]$$

where $I_{\parallel}$ is the equivalent integral molar absorption coefficient for ideally oriented OH groups, in a direction parallel to the electric vector of a plane IR polarized beam.

Then,

$$C_{\mathrm{OH\,liter}^{-1}} = \Delta(\mathrm{cm}^{-2})/I = \Delta(\mathrm{cm}^{-2})/\gamma I_{\parallel}. \qquad [2]$$

If this value is expressed in terms of OH number group per carrier atom, (Al + P), we have

$$C_{\mathrm{OH/(Al+P)ppm}} = (10^6\, M/2 \times 10^3\, d)(\Delta/\gamma I_{\parallel}), \qquad [3]$$

or

$$C_{\mathrm{OH/(Al+P)ppm}} = 0.322\Delta/\gamma, \qquad [4]$$

with

$-M$ = molar weight → $\mathrm{AlPO_4}$ = 122 g

$-d$ = density → 2.634 for berlinite.

Next, the anistropy factor, γ, for berlinite crystals must be determined.

Determination of the Anisotropy Factor, γ

This determination was based on the work of Kats (15) with regard to quartz. Considering the θ angle between the OH bonds and the c-axis, and using a beam perpendicular to the c-axis, the following anisotropy factors have been proposed:

—beam polarization $\parallel$ to c-axis →
$\gamma = \cos^2\theta \rightarrow$ absorption $= K_{\parallel}$

—beam polarization $\perp$ to c-axis →
$\gamma = 1/2 \sin^2\theta \rightarrow$ absorption $= K_{\perp}$.

TABLE 2
Infrared Absorption from a Berlinite Bar in Terms of Infrared Beam Direction and Polarization Direction

Beam direction	Polarization	K_1[a]	K_2[b]
$\parallel$ to a-axis	$\perp$ to a-axis	1.81	1770
	$\parallel$ to a-axis	1.96	1880
$\parallel$ to c-axis	$\perp$ to a-axis	1.235	1270
	$\parallel$ to a-axis	1.3	1310

[a] $K_1 = 1/d(A_{3300} - A_{3800})$.
[b] $K_2 = 1/d\int_{2500}^{4000} A(\nu)\, d\nu$.

For absorption bands of α-quartz located at 3435 and 3371 cm^{-1}, the value of the ratio found at 78 K is

$$R = K_{\perp}/K_{\parallel} = 6.5 = 1/2\, tg^2\theta \qquad [5]$$

and corresponds to a θ value of 75°. On the other hand, this R ratio converges to 1 when the hydroxyl content increases, showing that the OH distribution is becoming isotropic (18).

Consequently, this method has been applied to berlinite crystals, the absorption being computed either from the difference between A_{3300} and A_{3800} or from the integrated peak between 2500 and 4000 cm^{-1}. The results are summarized in Table 2 (see experimental details in the next paragraph).

From these values and assuming that OH groups make preferentially a θ angle with the c-axis, the anisotropy factors corresponding to each possibility have been computed and are given in Table 3.

TABLE 3
Computed Anisotropy Factors for Berlinite Crystals

Infrared beam direction	Polarization	Anisotropy factor
$\parallel$ to c-axis	In all cases	$1/2 \sin^2\theta = 0.326$
$\parallel$ to a-axis	$\parallel$ to c-axis	$\cos^2\theta = 0.349$
	$\perp$ to c-axis	$1/2 \sin^2\theta = 0.337$
	Without	$1/2 \cos^2\theta + 1/4 \sin^2\theta = 0.326$

Regardless of the experimental conditions (polarization), we can observe that the anisotropy factor brings up a constant value close to 1/3, corresponding to an

TABLE 4
Different Formulas Proposed to Quantify the –OH Content in Berlinite

	Isotropic hypothesis	Anisotropic hypothesis
Integral absorption 2500–4000 cm^{-1}	$C_{\mathrm{OH/(Al+P)ppm}} = 0.966\Delta$	$C_{\mathrm{OH/(Al+P)ppm}} = 0.322\Delta/\gamma$
Absorption band at 3300 cm^{-1}	$C_{\mathrm{mole\,liter^{-1}}} = K/\varepsilon$ (ε = 25.5 liter $\mathrm{mole}^{-1}\,\mathrm{cm}^{-1}$) $C_{\mathrm{OH/(Al+P)ppm}} = 907\ K$	$C_{\mathrm{OH/(Al+P)ppm}} = 302\ K/\gamma$

isotropic distribution of OH bonds. Indeed, the R ratios, previously defined, can be considered as equal to 1:

—infrared beam ⊥ to c-axis $R_1 = K_{1\perp}/K_{1\|} = 0.95$
$R_2 = K_{2\perp}/K_{2\|} = 0.97$

—infrared beam ∥ to c-axis $R_1 = 0.93$ $R_2 = 0.94$.

Thus, we can assume that the distribution of the OH group in the berlinite crystals is isotropic. Then, regardless of the polarization and the direction of the infrared beam, $\gamma = 1/3$ and Eq. (4) becomes

$$C_{\mathrm{OH/(Al+P)ppm}} = 0.966\Delta, \qquad [6]$$

where Δ is the absorption coefficient integrated between 2500 and 4000 cm^{-1}.

If only the absorption band at 3300 cm^{-1} is taken into account instead of the integral term, the ε value must be known. As previously specified,

if $C_{\mathrm{OH(mole\,liter^{-1})}} = K/\varepsilon = \Delta/I$ (with $K = A/d$), then
$$\varepsilon = IK/\Delta$$

On the other hand, $I = \gamma I_{\|} = 1/3 \cdot 72{,}000 = 24{,}000\ \mathrm{cm}^{-1}$. From experimental measurements, with $K = (A_{3300} - A_{3800})/d$, an average value,

$$\Delta/K = 940\ \mathrm{cm}^{-1},$$

can be obtained and then, $\varepsilon = 25.5$ liter $\mathrm{mole}^{-1}\ \mathrm{cm}^{-1}$, a value which is much lower than the other ones known (Table 1). Then,

$$C_{\mathrm{OH/(Al+P)ppm}} = 907K. \qquad [7]$$

We have summarized, in Table 4, the different formulas that we propose to quantify the OH content of berlinite crystals. These formulas have been applied to the infrared measurements of a berlinite crystal, and are compared with other formulas previously defined in Table 1.

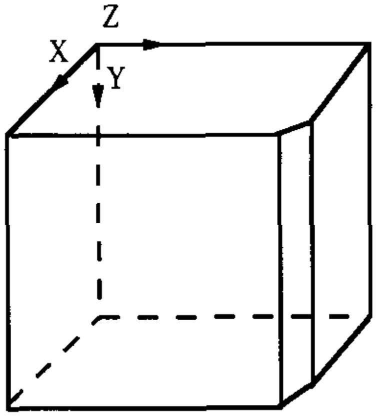

FIG. 1. Shape of the berlinite sample used for the infrared study (6.0 mm along X, 12.2 mm along Y, and 10.0 mm along Z).

III. APPLICATION TO THE IR MEASUREMENTS OF A BERLINITE BAR

III.1. Experiments

III.1.1. Sample. The bar investigated is a parallelepiped proceeding from a crystal obtained through hydrothermal crystal growth by the vertical temperature gradient method (14).

Its geometrical characteristics are given in Fig. 1 and its situation with regard to the seed is shown in Fig. 2. In order to compare easily the different methods, we have chosen a crystal with a high OH content.

III.1.2. Infrared spectrometer. The infrared spectrometer is a Fourier transform Brucker IF S113. Infrared measurements have been undertaken at room temperature, under vacuum, with a 1- × 2-mm diaphragm in the X and Y direction, Fig. 1 (X, Y, and Z are three cartesian axes. Z and X correspond to the c and a crystallographic axes, respectively).

III.2 Results

All the spectra are rather similar (Fig. 3) and the molecular water content at 5200 cm^{-1} is weak. On the other hand,

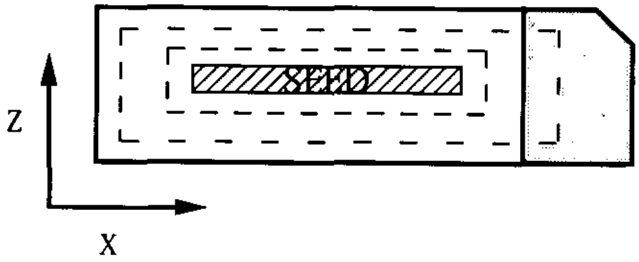

FIG. 2. Schema showing the position of the investigated berlinite bar with regard to the seed.

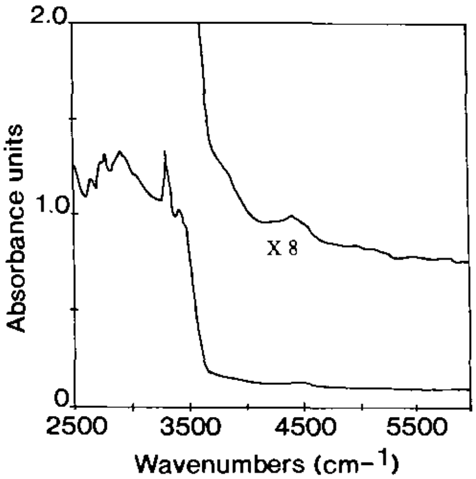

FIG. 3. Example of an IR absorption spectrum of the berlinite bar (incident beam parallel to the *Z*-axis). The upper NIRS has a magnified scale (× 8).

the existing –OH groups (3000–3500 cm^{-1}) are only due to hydroxyl groups *M*–O–H (*M* = Al, P, or an impurity) characterized by the absorption band centered on 4200 cm^{-1}.

III.2.1. Comparison between the different methods. The –OH content has been computed from the different methods previously described. The corresponding results, for the same part of the crystal, are summarized in Table 5.

These results show that the two methods, using the integration of the absorption band or its height peak, lead to very similar OH concentrations (Table 5). This seems to demonstrate a rather good and equivalent accuracy of these two calculations. Furthermore, these results are close to those obtained from the expression proposed by Boulognè *et al.* (28). This was expected because this method is rather similar to those used in our work with the integral absorption coefficient. Nevertheless, the relation of Boulogne *et al.* leads to slightly higher C_{OH} values. In fact, these authors have just transposed the formula given by Paterson (21) for quartz basal samples.

On the other hand, the formula suggested by Steinberg *et al.* (12) gives much lower C_{OH} values. This important gap registered with our results can be explained by the fact that these authors have used a C_{OH} relationship obtained from an equation used to evaluate the water content in boron oxide.

Thus, we think that the new proposed formula is adequate for berlinite and, given that the height peak method is easier to use, we chose this one to quantify OH content in berlinite crystals.

III.2.2. –OH distribution in the bar of berlinite. The bar of berlinite, previously described, has been investigated in *X* and *Z* directions, using the 3300 height peak method, ($C_{\mathrm{OH/Al+P\,ppm}} = 907\ (A_{3300} - A_{3800})$) to follow the –OH distribution during the growth. The results are given in Figs. 4 and 5. On the bell-shaped curve (Fig. 4), the –OH content is in the range 900–1400 ppm. The maximum

TABLE 5

Comparative Results of the OH Content for the Same Part of a Berlinite Crystal (Units: OH/(Al+P)ppm)

Formula	$C = 48.73\ \alpha$ (12)	$C = (1.07 \int T(\nu) d\nu / I(\nu))/d$ (28)	$C = 907(A_{3300} - A_{3800})$ (this work)	$C = 0.966\Delta$ (this work)
IR beam ‖ to *a*-axis, polarization ‖ to *c*-axis	595	1895	1650	1710
IR beam ‖ to *a*-axis, polarization ⊥ to *c*-axis	645	2015	1785	1820
IR beam ‖ to *c*-axis, polarization ‖ to *a*-axis	403	1365	1120	1230
IR beam ‖ to *c*-axis, polarization ⊥ to *a*-axis	427	1405	1185	1270

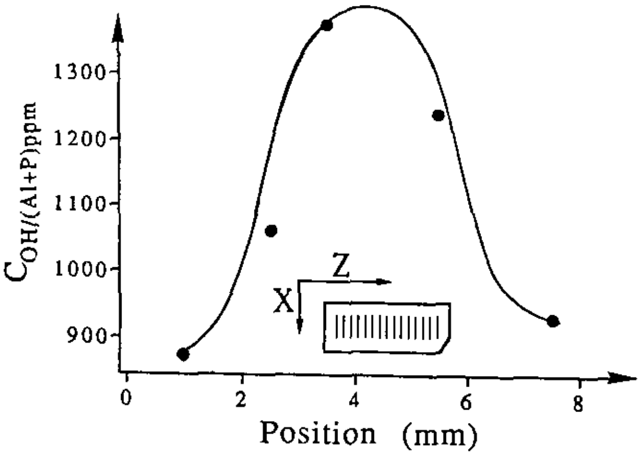

FIG. 4. Step scanning of the OH content of the berlinite bar in the *XZ*-plane, along a direction parallel to the *Z*-axis (see Fig. 2).

value corresponds to the central part of the crystal, that is, for the nearest part of the seed. On the other hand, a continuous decrease of the –OH content can be observed when the seed distance increases (Fig. 5). The faster diminution observed in the *Z* direction can be explained by the fact that the V_z growth rate (0.11 mm/day · face) is weaker than the V_x one (0.34 mm/day · face), knowing that the C_{OH} increases with the growth rate (14).

CONCLUSION

After an overview of the different IR methods used to quantify the OH content in α-quartz and berlinite crystals, we have proposed, from our IR study of a small bar of berlinite single crystal, a new relation for OH concentration determination (Eq. 7). Thus, the IR spectrometry shows a gradual decrease of the OH concentration when the seed distance increases. Furthermore, the OH decrease is emphasized following the *Z* direction where the growth rate is lowered in relation to the *X* direction.

On the other hand, in our field, investigating quartz analog materials MXO_4, we now apply this method to $GaPO_4$ available crystals.

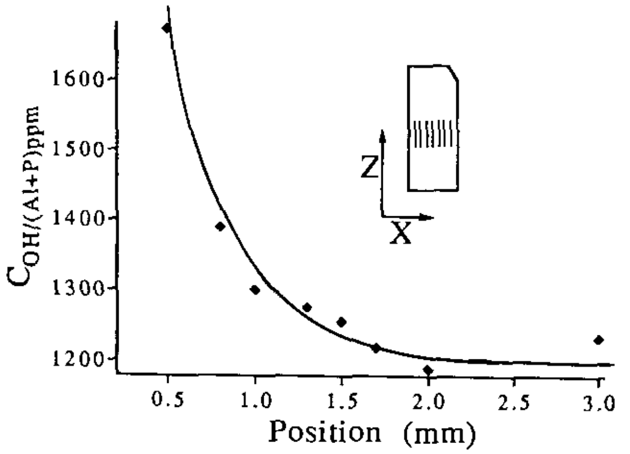

FIG. 5. Step scanning of the OH content of the berlinite bar in the *XZ*-plane and following a direction parallel to the *X*-axis (see Fig. 2).

ACKNOWLEDGMENT

The authors thank Pr. M. Galtier for the use of the IR spectrometer in his laboratory and for his useful comments.

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