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Infrared spectra of analyzed samples of the amblygonite–montebrasite series: a new rapid semi-quantitative determination of fluorine

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Abstract

Twenty-six analyzed samples in the amblygonite–montebrasite series $LiAlPO_4(F_{1-x}OH_x)$ and one of tavorite $LiFePO_4(OH)$ have been investigated by infrared spectroscopy in the 4000–300 cm^{-1} region. The 830–800 cm^{-1} band is reassigned to a bending vibration of the OH group. For the two bands near 3400 and 800 cm^{-1} corresponding to OH vibrations, both intensity and frequency depend on the fluorine content. For each of these bands, the IR frequency varies linearly with fluorine percentage, thus affording a quick semi-quantitative fluorine determination. No such relationship is found for the band intensity.

Introduction

Recent studies have attempted to correlate the physical properties of the amblygonite–montebrasite $LiAlPO_4(F_{1-x}OH_x)$ series with OH,F substitution. These studies have been initiated because of increasing economic interest of these minerals as a source of lithium, the potential petrogenetic significance of their occurrence, and the difficulties of chemical analysis.

Despite the scattering of the existing data, Winchell and Winchell (1951) proposed that variations of the optical properties (n, $2V$) correspond to changes in fluorine percentage. Moss *et al.* (1969) have shown that the a, b, c, α, β and γ cell parameters vary systematically with fluorine percentage and have established that the fluorine percentage is a function of the position of the $d(131)$ reflection. More recently, Dubois *et al.* (1972) attempted to revise the Winchell diagram but finally adopted the method proposed by Moss *et al.* (1969). Likewise, X-ray diffractometry was employed by Černá *et al.* (1973), who suggested several relationships between fluorine content and the position of six diffraction lines. All these relationships are related to samples with sodium substitutions of less than 1.5 weight percent.

Based on a reinterpretation of the IR spectrum of amblygonite, a new method is presented for determining the fluorine content by monitoring the variation of OH absorption bands.

Experimental

Source of the samples

Twenty-six analyzed samples of the amblygonite–montebrasite series were investigated by IR spectroscopy. Table 1 presents locality information and the origin of each specimen used in this study.

Infrared technique

The conventional pressed-disc technique has been used for the preparation of the samples: 2.5 mg of mineral were carefully ground and mixed with 0.6 g KBr, and this mixture pressed so as to give a disc of 20 mm diameter. Very careful grinding and mixing is essential in avoiding spurious effects such as a broadening of the bands and/or a frequency shift of the absorption maxima. All spectra have been registered between 4000 and 300 cm^{-1} with a Beckman IR 12 spectrophotometer. A few Raman spectra have also been registered.

Previous work on the IR spectrum of amblygonite

There is little doubt about the assignment of the high-frequency band (in the 3400–3350 cm^{-1} region)

Table 1. Source of specimens

Number	Locality
Specimen obtained from Dr O. Von Knorring (Von Knorring, 1970)	
246	Byasha mine, Uganda.
419	Benson 3 mine, Mtoko, Rhodesia.
420	Benson 2 mine, Mtoko, Rhodesia.
421	Benson 1 mine, Mtoko, Rhodesia.
524	Maridge mine, Muiane area, Alto Ligonha, Mozambique.
528 and 669	Wampewo, Uganda.
"Tavorite"	Karibib, S.W. Africa.
Specimens obtained from Prof. P. Černý (Černá *et al.*, 1973)	
A-1, A-2, A-3, A-4, A-13, A-22, A-29, A-60, A-98	Tanco Pegmatite, Bernic Lake, Manitoba, Canada.
AF-43	Nesbitt spodumene mine, Gunnison County, Colorado.
AF-44	Moguk, Upper Burma.
AF-46	Karibib, S.W. Africa.
AF-47	Plumbago, Newry, Maine.
AF-50	Coolgardie, West Australia.
Specimens investigated by J. Dubois (Dubois *et al.*, 1972)	
4545	Buranga Pegmatite, Rwanda.
16111	Keystone, South Dakota.
16445	Kobokobo Pegmatite, Kivu, Zaire.
16446	Kobokobo Pegmatite, Kivu, Zaire.
128227	Ilbini, Australia.

to the stretching motion of the OH group and of the strong absorption bands near 1100–100 cm^{-1} to the antisymmetric vibrations of the PO_4 ion. However, the assignment of the band observed in the 850–800 cm^{-1} region is less certain: this band has been assigned in turn, either to the symmetric stretching vibration ν_1 of the PO_4 tetrahedra (Correia Neves *et al.*, 1968) or to a stretching vibration of AlO_4 tetrahedra (Ross, 1974). The assignment of this band to the ν_1 symmetric stretch of the PO_4 ion seems improbable for the following reasons: (1) The frequency value is low, considering that ν_1 (PO_4) is generally observed in the 1000–900 cm^{-1} region. (2) However, the *intensity of the band* is high. The ν_1 mode is IR-forbidden for a true T_d symmetry, but if the tetrahedron is distorted, this mode becomes IR-active with an intensity which is generally low to very low. Conversely, ν_1 generally gives a strong peak in the Raman spectrum, but we have not observed such peak between 900 and 800 cm^{-1} in the Raman spectrum of amblygonite.

The assignment of the 815 cm^{-1} band of amblygonite to a vibration of an AlO_4 group (Ross, 1974) is untenable: the existing structural data (Simonov and Belov, 1958; Baur, 1959) agree on the presence of *octahedral* (and not tetrahedral) coordination of aluminium. Octahedral coordination produces bands at lower frequencies, namely 650–600 cm^{-1}, but not 800 cm^{-1} (Tarte, 1967a). Moreover, a similar band is observed near 800 cm^{-1} in the IR spectrum of the corresponding iron compound $LiFePO_4(OH)$ (tavorite), and this is also in contradiction with the assignment of this band to an Al–O vibration.

Comparison of tavorite, amblygonite, and montebrasite in spectra: new general assignments

Representative spectra are given in Figures 1 and 2. The observed frequencies are tabulated in Table 2. In view of the complexity of the structure and IR spectrum, a detailed interpretation would be difficult. However, we have found that there is a systematic change of the spectrum with a change in fluorine content. Also, by comparison to tavorite, some observations may be made concerning the assignment of bands and order–disorder relations.

The highest-frequency band near 3400–3350 cm^{-1} is assigned to the OH stretching vibration. This band exhibits characteristic behaviour, its frequency and intensity decrease, and its broadness increases, when the fluorine percentage increases. Likewise, there is

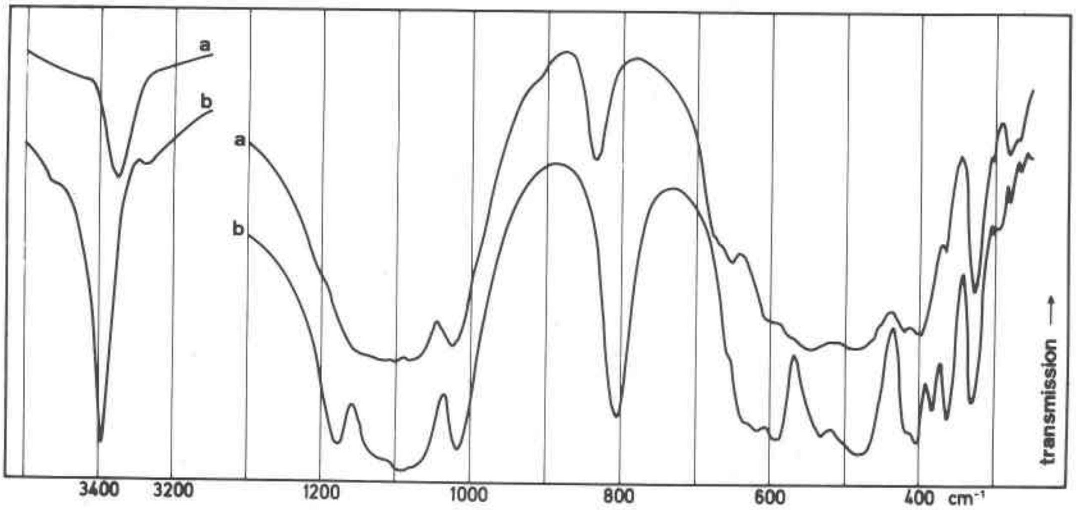

Fig. 1. Infrared spectrum of (a) amblygonite n°524 (9.57% F) (b) montebrasite n°AF-47 (0.30% F).

little doubt about the assignment of the group of strong bands in the 1200–1000 cm^{-1} region to the stretching vibrations of the PO_4 ion. The frequencies are lower by about 50 cm^{-1} in tavorite. However, when the fluorine percentage increases, these bands are significantly broadened, particularly for the high-frequency component near 1180 cm^{-1}. This band, which is reasonably sharp in montebrasite, becomes an ill-defined, very weak shoulder in amblygonite. Because the 1180 cm^{-1} band overlaps the strong 1100 cm^{-1} band and because this would make correlation with fluorine content difficult, the actual cause of this effect has not been investigated in detail.

The medium-to-low-frequency region (700–300 cm^{-1}) is also quite complex. Both PO_4 bending and AlO_6 stretching vibrations contribute to the absorption in the 650–500 cm^{-1} region. The effect of the Al–O bonds is suggested by comparison to the spectrum of the corresponding Fe compound (tavorite). Assuming an isostructural relationship, the Fe–O bonds in tavorite produce absorption bands at lower frequencies than Al–O bonds (Tarte, 1965) in amblygonite and montebrasite. In addition, the Li–O bonds should also contribute to the absorption near and below 500 cm^{-1} (Tarte 1964; 1967b), and finally, OH bending vibrations in this region are also possible. Clearly, the assignment problem in this region cannot be solved without further study of synthetic isotopic molecules (OH–OD; ^6Li–^7Li).

A new assignment of the 830–800 cm^{-1} band may be deduced from the following observations. (1) The intensity of the band decreases and its broadness increases with the increase of fluorine content. These variations are similar to those observed for the OH

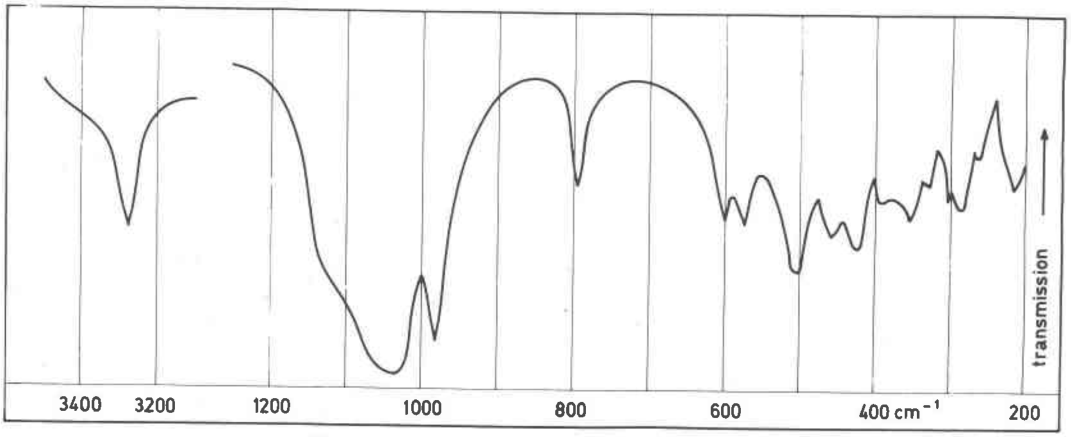

Fig. 2. Infrared spectrum of tavorite from Karibib.

Table 2. Infrared spectra of amblygonite, montebrasite, and tavorite. List of observed frequencies (cm^{-1})

a	b	c
		303
326	330	330
364	363	350
	384	
397 b	404	390
420 b	416 s	423
		458
485 b	480	
		502
545 b	532	
	592	575
600 s	618	600
650	655 s	
833	805	796
		982
1025	1018	1035
	1075	
1100 b	1095	1100 s
1200 s	1177	
3350	3391	3288

s = shoulder; b = broad.

a) Amblygonite, Alto Ligonha n°524 (9.57% F);
b) Montebrasite, Newry n° AF-47 (0.30% F);
c) Tavorite, Karibib.

band near 3400 cm^{-1}. (2) The frequency increases with fluorine percentage[1] (as compared with a decrease of the OH frequency near 3400 cm^{-1}). It is well known that, for structurally or chemically related compounds containing hydrogen-bonded OH groups, a decrease of a OH stretching frequency (corresponding to the shortening of the hydrogen bond) is associated with an increase of the corresponding OH bending frequency (Fig. 3) (Tarte, 1958). In view to these correlations, this band is assigned to the OH bending vibration, an assignment which is also consistent with the presence of a similar band (796 cm^{-1}) in the spectrum of tavorite.

There is an overall broadening of the entire spectrum as OH is progressively replaced by F. This broadening is more noticeable for some bands (see above) but is present to some degree in the whole spectrum. Three explanations may be proposed. (1) The broadening may be related to the statistical distribution of the $(OH)^-$ and F^- ions over the available sites. Such a distribution may, by itself, be responsible for a small broadening of some bands. Since the OH group is engaged in a hydrogen bridge O–H · · · · O (as revealed by the values of the OH stretching frequency), the OH,F replacement may have some influence on the position of the adjacent oxygen atoms, thus increasing the disorder effect and the broadening of the IR bands. If, however, the broadening is related to the statistical distribution of $(OH)^-$ and F^- ions, the spectrum should be sharp for the fluorine-rich samples. This is apparently not the case; the bands increase in diffuseness up to the fluorine-richest sample $LiAlPO_4(F_{0.75}OH_{0.25})$ available to us. (2) Alternatively, some oxygen atoms may be more tightly bonded (through the formation of hydrogen bonds) in the hydroxyl phase than in the fluorine phase. Hence, small positional disorder may be occuring. (3) Baur (1959) has suggested the possible existence of two forms of amblygonite to explain differences between the structures determined by

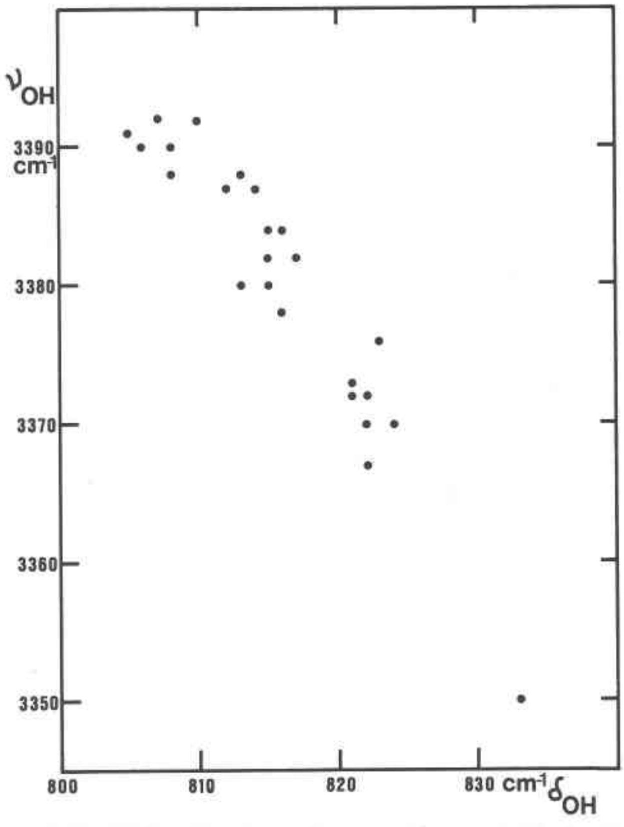

Fig. 3. Relationship between the ν_{OH} and δ_{OH} frequencies in the amblygonite–montebrasite series.

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[1] Our results on both frequency and intensity conflict with the data published by Ross (1974). He has found that the intensity is lower and the frequency higher for the OH end-member than for the F end-member. Although the possibility of "anomalous" samples cannot be ruled out, detailed chemical analyses are not available for the samples investigated by Ross.

himself and by Simonov and Belov (1958). The latter structure differs from that of Baur's by the statistical distribution of lithium over two slightly offset positions. Unfortunately, detailed chemical analyses are not provided for these samples, and it is possible that the structural differences are related to differences in chemical composition. Compositional differences are suggested by Moss *et al.* (1969) and Černá *et al.* (1973): the mineral investigated by Simonov and Belov would be a montebrasite. This supports the contention that high fluorine content may be correlated with positional disorder of lithium.

In conclusion, our IR data strongly support the hypothesis of a disordering phenomenon in some minerals of the amblygonite–montebrasite series, the degree of disorder being related to the fluorine percentage. However, the actual nature of this disorder is still to be elucidated.

Application of the IR spectra to the semi-quantitative determination of fluorine

In the preceding part of this paper, the two bands near 3400 and 800 cm^{-1} have been found to vary in both position and intensity with fluorine content (Table 3). Since these bands are isolated in the spectrum and relatively free from overlapping with other bands, they are well suited for an investigation to determine a relationship between their intensity or their frequency, and the fluorine percentage.

Table 3. Fluorine content and infrared frequencies δ_{OH} and ν_{OH} (cm^{-1})

Specimen number	% F	δ_{OH}	ν_{OH}
AF-47	0.30	805	3391
420	1.14	808	3390
A-22	1.40	806	3390
AF-44	1.45	808	3388
AF-43	1.88	810	3392
669	2.12	812	3387
16111	2.90	812	3387
16445	3.00	815	3384
421	3.20	816	3384
A-98	3.44	815	3384
528	3.61	814	3387
A-4	3.65	815	3382
A-2	3.65	813	3380
16446	4.10	815	3380
4545	4.40	816	3378
246	4.41	817	3382
A-1	5.56	821	3372
128227	5.80	822	3367
A-60	6.17	820	3370
A-29	6.30	820	3370
A-3	6.30	822	3370
419	6.36	823	3376
A-13	6.43	822	3372
AF-50	7.07	821	3373
AF-46	7.24	824	3370
524	9.57	833	3350

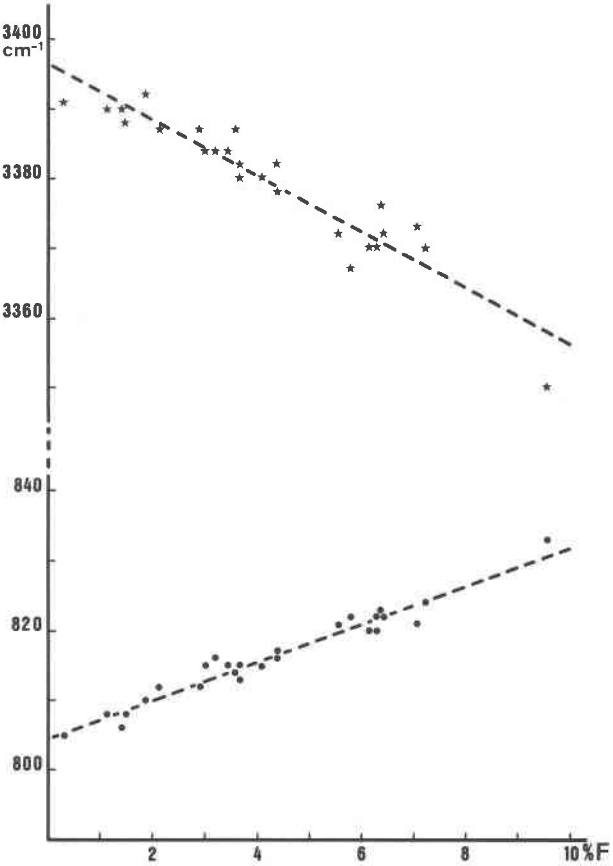

Fig. 4. Frequencies ν_{OH} (upper curve) and δ_{OH} (lower curve) *versus* fluorine content in the amblygonite–montebrasite series.

A plot of fluorine percentage as a function of the observed frequency of these bands gives a linear relationship as illustrated in Figure 4. The best-fit equations as calculated by the least-squares method are expressed by:

$$\delta_{OH} = (2.74\,x + 804.6)\ cm^{-1} \qquad (1)$$

$$\nu_{OH} = (-4.06\,x + 3396.5)\ cm^{-1} \qquad (2)$$

where x is the fluorine percentage (expressed in weight percent) and δ_{OH} and ν_{OH} are the observed bending and stretching frequencies of the OH group, respectively. The linear correlation coefficients are 0.971 and 0.944 for equations (1) and (2) respectively. Thus, a careful measurement of the δ_{OH} and ν_{OH} frequencies leads, through the use of equations (1) and (2), to a semi-quantitative determination of the fluorine percentage.

The method is rapid and simple. Its limitations and drawbacks may be summarized as follows:

(1) Because of the broadness of the bands, the error associated with the frequency measurements is ±2 cm^{-1} for the δ_{OH} band and ±4 cm^{-1} for the ν_{OH} band. The corresponding average error on the fluorine percentage is ±0.37 (δ_{OH}) or ±0.5 (ν_{OH}).

(2) The relationship is not as straightforward as it should be: the OH content has *not* been determined experimentally (except for a few samples given by Professor Černý) but instead has been deduced from the experimental fluorine content. It should be pointed out that this relationship between the OH and F content is valid only if no significant amounts of other substituents (Na for Li; Fe for Al) are present in the sample.

(3) Because the investigated samples were low in Na_2O (less than 1.5% by weight), equations should be restricted to similar compositions. Any significant amount of Li,Na (or Al,Fe) replacement should modify the position of the OH bands.

We also attempted to determine if there is a relationship between the intensity of the OH bands and the fluorine (or H_2O when available) percentage. However we could not obtain significant results by using the base-line method (*e.g.* Tarte and Deliens, 1973), as the points were very scattered around an apparently non-linear relationship. The degree of scattering is the same, whatever the band (3400 or 800 cm^{-1}), the method of intensity measurement (maximum or integrated absorption), or the composition variable (F amount or H_2O amount when available. The samples were carefully prepared (weighing, grinding, and disc pressing), therefore the preparation is not believed to be the cause for the observed scattering. We tentatively propose that this could be related to a variable degree of disorder or structural distortions which is otherwise suggested, either by X-ray studies (Baur, 1959) or by the observed broadening of IR bands (this work).

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