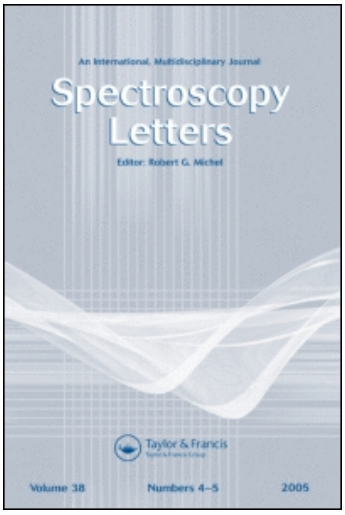

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Raman Investigations of Biselenates. The Raman Spectra of $RbHSeO_4$ in the Range 20-300K

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RAMAN INVESTIGATIONS OF BISELENATES. THE RAMAN SPECTRA OF $RbHSeO_4$ IN THE RANGE 20-300K

Key words: Raman spectra, $RbHSeO_4$, ferroelectrics

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Introduction

In 1977 we undertook investigations[1] of the Raman spectra of $RbHSeO_4$ and NH_4HSeO_4, prior to the discovery of their ferroelectric nature by a group of workers in Poland.[2,3] Our studies did not reveal some of the behavior reported by this group, and other studies[4,5] have indicated phase transitions not observed by us or the Polish group.[6-9] Consequently we have withheld publishing the results of our earlier studies pending the completion of investigations designed to verify our initial findings and to determine the relationships between our Raman spectra and the reported behavior of these compounds. This paper represents the first in a planned series of communications relating our experiences with these biselenates and our interpretations of those

points of disparity between the various studies that have been reported.

$RbHSeO_4$ shows a phase transition from a paraelectric to a ferroelectric phase when cooled below its Curie point, T_c = 370.6K.[2,4] X-ray studies suggest that the transition is first order[10] from a monoclinic lattice (P2, Z = 3) in the paraelectric phase[11] to a triclinic lattice (P1, Z = 3) in the ferroelectric phase.[12] The pseudo-orthorhombic nature of the structures and their similarity to the non-isomorphous structures of $RbHSO_4$ and NH_4HSO_4 prompted Waśkowska, et al.[11,12] to choose unit cells with Z = 6 in the unconventional settings I2 and I1, respectively. The factor group selection rules on which the infrared and Raman spectra depend, however, are based on the primitive cells, making the conventional settings more useful for spectroscopic discussions. The present study concerns the Raman spectra of $RbHSeO_4$ in the temperature range 20-300K, where the compound is presumably ferroelectric. Results of our investigations from room temperature to above the phase transition point (>98°C) will be presented in a separate paper.

Baran, et al.[13] recently published single-crystal Raman data and infrared data from Nujol mulls and KBr pellets for $RbHSeO_4$ and $RbDSeO_4$. All spectra were obtained at room temperature. Reference in the abstract of that paper to data obtained at 383K is apparently to room-temperature infrared spectra of samples that

had undergone prior heating to high temperature. The infrared results have limited value since selenates react strongly with the window materials in both pellets and mulls. Consequently the Raman data are most useful in discussing the relationships between vibrational spectra and crystal structure. It should be pointed out, however, that the usual direct comparisons between the spectra of deuterated and non-deuterated homologous compounds cannot be made in this case, because $RbHSeO_4$ and $RbDSeO_4$ are not isomorphous.[14] Our Raman studies on polycrystalline samples of $RbHSeO_4$ at room temperature agree in most important aspects with those of Baran, et al. The low temperature results, however, reveal some aspects which are not evident at higher temperatures.

Experimental

Our experience in synthesizing both $RbHSeO_4$ and NH_4HSeO_4 leads us to the conclusion that samples of high purity are not obtained by most aqueous methods.[1] Analyses of samples prepared by the classical method of Norris and Kingham[15] invariably showed significantly low values for H^+, suggesting coprecipitation of $SeO_4^=$ with $HSeO_4^-$. Purity problems seemed to increase with increasing size of the crystals obtained. The presence of selenate ion in water is unavoidable, since $K_2 = 1.2 \times 10^{-2}$ for H_2SeO_4. Furthermore, the tendency of $SeO_4^=$ and $HSeO_4^-$ to coprecipitate can be seen in the existence of well-characterized compounds such as $(NH_4)_2SeO_4 \cdot 2NH_4HSeO_4$[16] and the ferroelectric $(NH_4)_3H(SeO_4)_2$.[17]

Another complication arises from the oxidizing potential of selenate ion in acid:

$$SeO_4^{=} + 8H^{+} + 6e^{-} \rightarrow Se + 4H_2O \qquad E^{O} = +0.88v$$

Although selenate ion appears to be a generally sluggish oxidant, it is sufficiently strong to oxidize NH_4^{+} to N_2. This becomes important in preparing crystals of NH_4HSeO_4 by slow evaporation, where the appearance of a faint pink coloration in the product indicates formation of elemental selenium. One consequence of this is sample incineration in the beam of an argon laser at either 514.5nm or 488.0nm. Of course this is less of a problem in preparing $RbHSeO_4$, but the presence of trace impurities of oxidizable material can lead to noticeably discolored product.

We have found that coprecipitation and redox problems can be avoided by mixing reactants in a medium of glacial acetic acid. The lower dielectric constant and higher acidity of this solvent suppress the second dissociation of selenic acid, while the lower solubility of the product causes rapid crystallization, which minimizes redox produced impurities. Production of acetate salts does not appear to be a problem. Analysis for H^{+} by titration gives values which deviate by less than 1% from the expected values for the compounds synthesised (purity ≈99.5%). Our concern with purity arises from our experience with NH_4HSeO_4, where sample preparation method profoundly influenced temperature dependent changes in the Raman spectra.[1]

Samples of $RbHSeO_4$ for the present study were prepared by adding 2.5g of Rb_2CO_3 to a solution containing 20ml of 3.95M H_2SeO_4 in 200ml of glacial acetic acid. The solution was heated to 60°C to facilitate dissolving. Following filtration through a medium sintered glass frit, the cooled solution was allowed to stand over $CaCl_2$ under reduced pressure. Crystals which formed overnight were collected by filtration, washed with glacial acetic acid, and dried over P_2O_5 *in vacuo*. An analogous synthesis using RbOH yielded equally pure product. Compared to crystals obtained by the usual aqueous method, $RbHSeO_4$ prepared from acetic acid seems to be less hydroscopic, shows superior stability on storage, and better withstands repeated heating above 120°C. X-ray examination shows that our samples have the same triclinic morphology found by Waśkowska, *et al.*,[12] as indicated in Table 1.

Raman spectra were obtained with a Spex Ramalog system with an add-on third monochromator, which functioned as a fixed-frequency variable bandpass filter below $200cm^{-1}$. The come-off point from the exciting frequency was typically $10cm^{-1}$. Most spectra were

TABLE 1

Structure Data at Room Temperature for $RbHSeO_4$ (I1, Z = 6)

Source	a	b	c	α	β	γ	V
Rev. 12	19.359	4.619	7.572	90.60	89.80	90.73	677Å^3
This work	19.328	4.611	7.567	90.27	89.87	90.74	674Å^3

excited with an argon laser operating at 514.5nm and 600-1100mw. Below $1000cm^{-1}$, where sharp bands are observed, the spectral bandpass was $1cm^{-1}$. Above $1000cm^{-1}$, where broad and weak bands due to OH motions are observed, the spectral bandpass was $2\text{-}3cm^{-1}$. Claasen filtration or a spike filter eliminated unwanted laser frequencies, but any remaining bands of suspicious origin were verified by examining spectra obtained with krypton laser excitation (647.1nm, 500mw). A Cryogenic Technology Model 20 Cryocooler equipped with a bucking heating system provided variable temperature setting throughout the range 20-300K. A brass or aluminum sample holder provided thermal contact between the cold station of the apparatus and the polycrystalline samples contained in sealed 0.9mm o.d. capillary tubes. Several hours elapsed between setting a desired temperature and obtaining data to ensure that the sample was in thermal equilibrium with the cold station, where the thermocouple is located.

The selection rules governing infrared and Raman activity in the P1 primitive cell of ferroelectric $RbHSeO_4$ are non-restrictive. Following the practice of Paetzold and Amoulong,[18] it is customary to assign the frequencies of $HSeO_4^-$ ions according to the system used for tetrahedral $SeO_4^=$, recognizing the descent in symmetry from T_d to C_{3v}. In the crystal, the remaing two-fold degeneracies of C_{3v} are lifted by the trivial C_1 site symmetry in the triclinic lattice,

and the motions of the three unique $HSeO_4^-$ ions may couple to give rise to 3(3N-6) internal modes active in both spectra. Additionally, there are 9 rotational external modes due to $HSeO_4^-$ and 15 translational external modes due to both $HSeO_4^-$ and Rb^+.

Results and Discussion

Figure 1 shows the spectrum of $RbHSeO_4$ at 20K in the region below $1000cm^{-1}$. Note that three different scales are represented in Figure 1, with highest instrumental amplification in the region below $200cm^{-1}$. Figure 2 shows the region of O-H stretching, ν(OH), and in-plane bending, δ(OH), at temperatures between 20K and 300K. The features at $1880cm^{-1}$ and $1960cm^{-1}$ result from the glass capillary. The relatively sharp band at $1570cm^{-1}$, which is most evident at low temperatures, appears to be genuine. Attempts to observe this band from capillary samples of K_2SO_4, $KHSO_4$, RbCl, and $RbC_2H_3O_2$ were unsuccessful. Tables 2-4 show the frequencies observed for $RbHSeO_4$ at 20K and 300K with proposed assignments. Standard deviations for the data are better than $\pm 1.1cm^{-1}$ below $1000cm^{-1}$, better than $\pm 6cm^{-1}$ in the region $1000-2000cm^{-1}$, and better than $\pm 7cm^{-1}$ above $2000cm^{-1}$. Owing to the breadth of the bands above $2000cm^{-1}$, frequencies for the A and B components of ν(OH) are limited to three significant figures.

Our room-temperature data agree in most respects with the results reported by Baran, et al.,[13] if

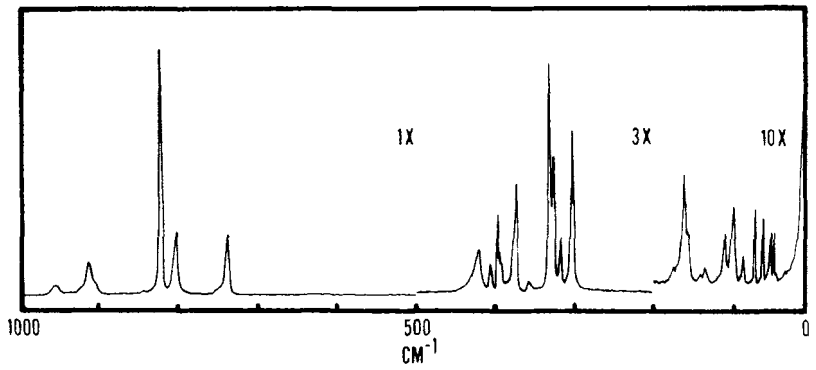

FIG. 1. Raman spectrum of $RbHSeO_4$ below $1000cm^{-1}$ at 20K.

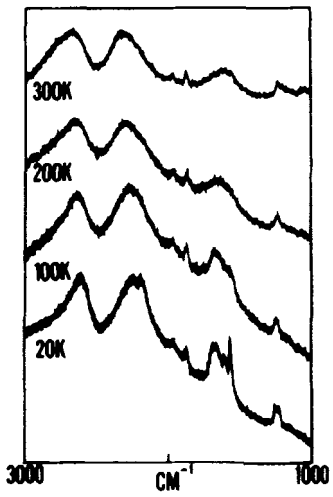

FIG. 2. Raman spectrum of $RbHSeO_4$ in the range $1000 - 2000cm^{-1}$ at temperatures between 20K and 300K.

allowances are made for the differences expected between polycrystal and single-crystal samples. Nonetheless, we cannot verify the weak and broad unassigned band at $250cm^{-1}$ which they have reported. Furthermore, in light of the stated $6cm^{-1}$ resolution of their study,

TABLE 2

Raman Frequencies (cm^{-1}) of $RbHSeO_4$ at 20K and 300K (above $1000cm^{-1}$)

20K	300K	Assignment
2620	2650	ν(OH)A
2250 2200	2300	ν(OH)B
1695 1667 1604	1620	ν(OH)C $2\nu_1$ (?)
1570		$\nu_1 + \nu_3$
1256 1233	1230	δ(OH)

TABLE 3

Raman Frequencies (cm^{-1}) of $RbHSeO_4$ at 20K and 300K (200 - $1000cm^{-1}$)

20K	300K	Assignment
959(sh) 955 920(sh) 913 904(sh)	954 916 908(sh)	ν_3 (E in C_{3v}) & γ(OH) (?)
844(vw)		$2\nu_4$
821 802	829 816(sh)	ν_1
750(sh) 739	745(sh) 733	ν_3 (A_1 in C_{3v})
430 420 405 397 394 391 373	420 405 397 375	ν_4
357 331 326 317 305	353 334 320 308	ν_2

TABLE 4

Raman Frequencies (cm^{-1}) of $RbHSeO_4$ at 20K and 300K (under $200cm^{-1}$)

20K	300K	Assignment
175(sh)		
163		
158	160	$HSeO_4^-$ libration
140		
136		
111		
100	98	translation or libration
89		
76	77	
	74	
67		
64	62	translation
54	55	
49	49	
46		
36	35	

we feel that all frequencies obtained from different orientations and separated by less than $3cm^{-1}$ should be regarded as accidentally degenerate. We agree with most of their assignments with some minor exceptions, which may be noted in Tables 2-4.

As the sample is cooled the Raman bands narrow and a great deal of structure becomes evident within envelopes. With some exceptions, frequencies tend to shift downward slightly, but there are no clear indications of a phase change within the temperature range of this study.

The most remarkable feature of the low temperature spectrum is a simplicity nearly consistent with a monoclinic structure. The low symmetry of both the triclinic and monoclinic structures for $RbHSeO_4$

would give rise to 27 internal modes (disregarding OH motions). However, a monoclinic structure, such as that of the paraelectric phase, places the ions on general (C_1) and special (C_2) sites in a 2:1 ratio of occupancy. At the limit of diminishing interionic interaction the site group selection rules become operative. For example, in the space group P2, the site group predictions are two frequencies of type ν_1, four frequencies of type ν_2, and 6 frequencies each of types ν_3 and ν_4. Furthermore, since the ratio of occupancy of general to special sites is 2:1, bands arising from similar motions of ions on C_1 and C_2 sites might be expected to show a 2:1 intensity ratio. We have found such a ratio of integrated intensities in at least three unambiguous band pairs: (136,140cm^{-1}), (331,326cm^{-1}), and (821,802cm^{-1}). Other examples are suspected but cannot be verified, owing to the uncertainty inherent in graphical resolution of complex band envelopes. The number of internal mode frequencies observed at 20K is nearly consistent with the suggested monoclinic site model, were it not for one "extra" component each of ν_2, ν_3, and ν_4, which it could be argued arise from minimal interionic vibrational coupling.

The apparent agreement of the low-temperature Raman spectrum of $RbHSeO_4$ with a monoclinic site model should not be taken alone as evidence for such a structure. Rather, the spectrum serves to emphasize the structural similarity between the paraelectric

(monoclinic) and ferroelectric (triclinic) phases. The loss of the two-fold axis in passing through T_c causes symmetry-related pairs of ions on general positions to become distinct. Our Raman results suggest that the distinction between these pairs of biselenate ions in the triclinic phase is slight - perhaps less than the X-ray data indicate.[12] Consequently, the triclinic structure might be described as pseudo-monoclinic.

The region of ν(OH) and δ(OH), above 1000cm^{-1}, exhibits some interesting changes with cooling (Figure 2). Typical of strongly hydrogen-bonded OH systems, ν(OH) appears as a three-band ABC system, arising from Fermi resonance with 2δ(OH) and 2ν(OH).[19-21] At 20K the B and δ(OH) bands are split into doublets. The splitting of the C band is more complex, owing to the appearance of a relatively sharp band at 1570cm^{-1} and a more diffuse band at 1604cm^{-1}. The 1570cm^{-1} band is too sharp to be a ν(OH) component and has been tentatively assigned to $\nu_1+\nu_3$. Its appearance on cooling results from narrowing and shifting of the C band. The band at 1604cm^{-1} may be a third component of the C band or $2\nu_1$. In any event, the splitting observed throughout this region may be interpreted as the superimposing of the spectra of essentially two types of OH bonds in the pseudo-monoclinic structure.

We have not observed a band which can be assigned

to OH out-of-plane bending, γ(OH), owing to interference from ν_1 and ν_3 bands. From the assignment[13] of γ(OD) to 625cm^{-1}, a $\sqrt{2}$ shift would suggest 884cm^{-1} as the location of γ(OH). However, this reasoning may be faulty, since $RbHSeO_4$ and $RbDSeO_4$ are not isostructural.[14] Odinokov and Iogansen[21] have developed a relationship by which γ(OH) can be estimated from the ABC band contour. Using this with our data, we expect γ(OH) at 900±25cm^{-1} in the temperature range of this study. Perhaps the weak band at 913cm^{-1} in the c(bb)a spectrum of Baran, et al. is this mode. We note, however, that for $RbHSO_4$, a non-isomorphous compound with similar hydrogen bonding, γ(OH) is found in the range 730-825cm^{-1}, depending on temperature and phase.[22]

The movement of the OH bands suggests strengthening of hydrogen bonding with cooling. It is expected that ν(OH) should shift down and δ(OH) and γ(OH) should shift up with increasing strength. Only the movement of the C band appears to be contrary to this. Since the maximum of this band is expected to be influenced by 2δ(OH), with which it is in Fermi resonance, the probable shift of δ(OH) to higher frequency may account for the observed shift in the C component.

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