

## Low-Temperature Raman Study on ThSiO<sub>4</sub> Single Crystal and Related Infrared Spectra at Room Temperature

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Before analyzing the optical spectra of some  $M^{4+}$  ions diluted in ThSiO<sub>4</sub>, Raman and infrared studies were undertaken on a single crystal of thorite. Indeed a strong coupling between the electronic transitions within the  $f$  band and the vibrations of the host lattice is expected. All the active modes of vibration at  $k = 0$  of ThSiO<sub>4</sub> were assigned in the  $D_{4h}$  point group. Raman scattering spectra recorded between 300 and 4.2 K have shown that the crystalline structure of thorite does not change down to 4.2 K. © 1986 Academic Press, Inc.

### Introduction

Thorium silicate, ThSiO<sub>4</sub>, is an attractive crystalline host for the study of the electronic structure of  $M^{4+}$  actinide ions by optical spectroscopy and these doped material may have some possibility in nonlinear optics and quantum electronics. The tetragonal transparent crystal stabilizes the 4+ oxidation state of the actinide ions substituted into the  $D_{2d}$  symmetry site of Th<sup>4+</sup>. Due to the highest radius of Th<sup>4+</sup> among the  $M^{4+}$  ions of the actinide series, the substitution can occur without distorting the neighboring environment.

For a complete analysis of the electronic and vibronic spectra, it is necessary to know the energy of the vibration modes of the ThSiO<sub>4</sub> lattice. Moreover, the optical spectra being recorded at 4.2 K we have to be sure that the crystalline structure of ThSiO<sub>4</sub> remains the same at low temperature. Therefore, Raman studies were performed at different temperatures varying from 300 to 4.2 K, as well as infrared absorption at room temperature.

Until recently, only the extensive Raman study of Syme *et al.* (1) has been published on the vibrational spectra of thorite, but this work was performed at 295 K only. On

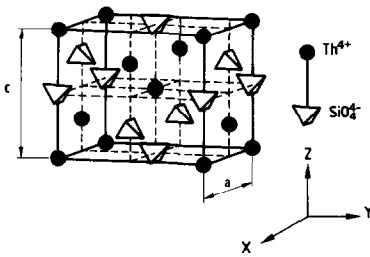


FIG. 1. The tetragonal unit cell of thorite in the space group  $D_{4h}$ .

the other hand, much more work (Raman and infrared studies) has been done on zircon,  $ZrSiO_4$  (2–5), and hafnon,  $HfSiO_4$  (6), both isomorphous with thorite.

### Theoretical Considerations

Thorite has a tetragonal crystallographic cell containing four units of  $ThSiO_4$  (Fig. 1). However, the primitive unit cell contains only two  $ThSiO_4$  formulas and leads to 36 normal modes of vibration at  $k = 0$ . They belong to irreducible representations of the point group  $D_{4h}$  and they are listed in Table

TABLE I  
NORMAL MODES OF THORITE IN THE POINT GROUP  $D_{4h}$  AND THEIR RAMAN AND INFRARED ACTIVITIES

Normal modes at $k = 0$							
$D_{4h}$	$N$	$N_{ac}$	$N_{int}$	$N_{ext}$		Activity	
				$N_{rot}$	$N_{tr}$	Raman	IR
$A_{1g}$	2	0	2	0	0	a	.
$A_{2g}$	1	0	0	1	0	.	.
$B_{1g}$	4	0	2	0	2	a	.
$B_{2g}$	1	0	1	0	0	a	.
$E_g$	5	0	2	1	2	a	.
$A_{1u}$	1	0	1	0	0	.	.
$A_{2u}$	4	1	2	0	1	.	a
$B_{1u}$	1	0	0	1	0	.	.
$B_{2u}$	2	0	2	0	0	.	.
$E_u$	5	1	2	1	1	.	a

Note.  $N_{int} + N_{ext} = N_{opt} = 2A_{1g} + 1A_{2g} + 4B_{1g} + 1B_{2g} + 5E_g + 1A_{1u} + 3A_{2u} + 1B_{1u} + 2B_{2u} + 4E_u$ .

I, where  $N$  represents the total number of modes,  $N_{ac}$  the three acoustic modes, and  $N_{opt}$  the optical ones. For the optic modes the distinction between internal ( $N_{int}$ ) and external ( $N_{ext}$ ) modes is due to the tetrahedral substructure of the tightly bound  $SiO_4$  molecular unit in the tetragonal structure of  $ThSiO_4$ . The internal modes involve oxygen–silicon motions within the tetrahedron and the external modes are concerned by  $Th^{4+}$  cation and  $SiO_4^{4-}$  unit motions. They can be subdivided into rotatory  $N_{rot}$  and translatory  $N_{tr}$  modes.

The Raman tensors for  $D_{4h}$  irreducible representations given by Loudon (7) are referred to the crystallographic axes  $X$ ,  $Y$ , and  $Z$  as follows:

$$\begin{array}{l}
 A_{1g} \begin{bmatrix} a & . & . \\ . & a & . \\ . & . & b \end{bmatrix} \quad B_{1g} \begin{bmatrix} c & . & . \\ . & -c & . \\ . & . & . \end{bmatrix} \\
 B_{2g} \begin{bmatrix} . & d & . \\ d & . & . \\ . & . & . \end{bmatrix} \quad E_g \begin{bmatrix} . & . & e \\ . & . & . \\ e & . & . \end{bmatrix}, \begin{bmatrix} . & . & . \\ . & . & e \\ . & e & . \end{bmatrix}.
 \end{array}$$

For infrared experiments, according to the selection rules, the  $A_{2u}$  and  $E_u$  modes are, respectively, allowed when the electric vector of the transmitted light is parallel and perpendicular to the fourfold crystallographic axis  $Z$ .

### Experimental

$ThSiO_4$  exists under two crystalline forms: huttonite with a monoclinic structure and thorite with a tetragonal habit which is only concerned with this paper. The phase transition temperature occurs around  $1225^\circ C$  (8), the thorite being the low-temperature phase.

Crystals of thorite were grown by the flux method following Chasse and Osmer (9). An equimolar mixture of  $ThO_2$ – $SiO_2$  was dissolved in a convenient solvent:  $Li_2MoO_4$ –

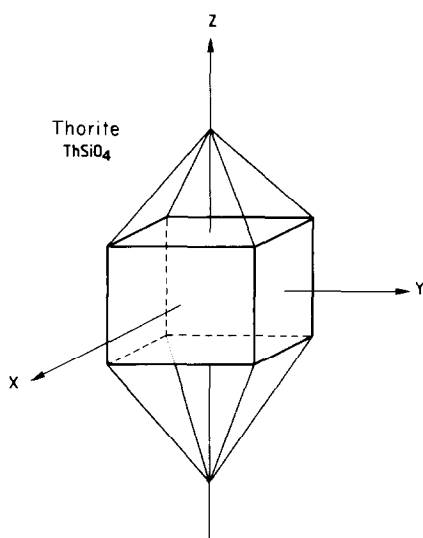


FIG. 2. Direction of the crystallographic axes  $X, Y, Z$  with respect to the macroscopic habit of thorite.

MoO<sub>3</sub> at 1150°C and slowly cooled down to around 800°C at a 1.5°C/hr rate. In these conditions, the supersaturated solution gives rise, after nucleation, to many well shaped single crystals, which do not exceed 2 mm in size.

The tetragonal structure of the obtained crystals was confirmed by X-ray analysis. The calculated cell parameters:  $a = b = 7.122 \pm 0.004 \text{ \AA}$  and  $c = 6.317 \pm 0.004 \text{ \AA}$ , are in good agreement with the literature values (10, 11). Moreover, the orientation of the crystallographic axes with respect to the tetragonal bipyramidal habit of the crystal, was checked using the Laue method (Fig. 2).

In the Raman experiments, the incident light was provided by a "Spectra Physics" cw argon laser, operating at 5145 Å. The 90° scattered light was analyzed by a "Coderg T 800" double monochromator. The incident and scattered light polarizations were determined by using Polaroid film. For an output polarization parallel to the grating lines, 100 mW of laser power was enough, but twice this power was necessary for the

opposite polarization. For the low-temperature experiments, we used an "Oxford Instrument" flow cryostat equipped with a temperature regulation device between 4.2 and 300 K.

The infrared absorption experiments were performed on a "Bruker 113 V" Fourier transformed spectrometer equipped with a pyroelectric DTGC detector for the 50- to 700-cm<sup>-1</sup> region and with a MCT (Hg-Cd-Te) detector above 500 cm<sup>-1</sup>. The resolution was chosen at 2 or 4 cm<sup>-1</sup> depending upon the wavenumber regions. The sample was in a crystalline powder form mixed with crude paraffin and pressed between two TPX plates for the 50- to 700-cm<sup>-1</sup> region and two KBr plates above 500 cm<sup>-1</sup>.

## Results and Discussion

### Raman

Figures 3 and 4 show the Raman spectra recorded at 300 and 4.2 K for different polarizations. The standard notation  $u(vw)t$  used for a specific geometry indicates that the incident light is directed along  $u$  and polarized along  $v$  and the scattered light is directed along  $t$  and polarized along  $w$ , where  $u, v, w, t$  are referred to the crystallographic axes  $X, Y, Z$ .

The low-temperature spectra recorded at 100 and 4.2 K (Fig. 4) are quite similar in frequencies to the room-temperature spectra (Fig. 3). The shift in energy never exceeds 2 cm<sup>-1</sup> for a same mode and the doubly degenerated E<sub>g</sub> modes are not split at 4.2 K. In that way, we are sure that no phase transition occurs at low temperature. Therefore, the site symmetry of thorium remains  $D_{2d}$  from 300 to 4.2 K.

A lack of polarization is observed in all spectra. It should probably be due to the small size of the crystal which makes difficult the crystallographic axes orientation and provides edge scattering. For the low-temperature experiments, the use of a win-

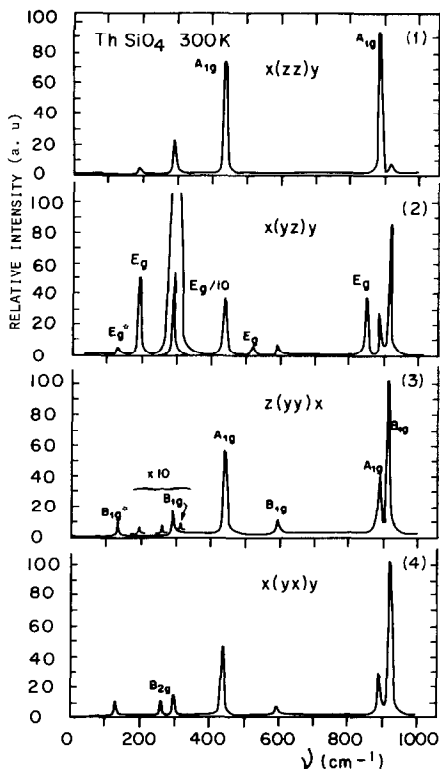


FIG. 3. Raman spectra of thorite recorded at room temperature for the four appropriate geometries: (1)  $X(ZZ)Y$ ; (2)  $X(YZ)Y$ ; (3)  $Z(YY)X$ ; and (4)  $X(YX)Y$ . \* Denotes a doubt in the mode assignment between  $B_{1g}$  and  $E_g$  symmetry.

dow cryostat increased the depolarization of the spectra. Consequently, we will consider only the room-temperature spectra for the latter discussion.

The lack of polarization is specially pronounced in spectra 3:  $Z(YY)X$  and 4:  $X(YX)Y$  in Fig. 3 which are concerned with the  $X$  and  $Y$  crystallographic axes. The same feature was noticed by Dawson *et al.* (2) who gave at that time an explanation pointing out that when these two axes are misorientated, the Raman tensors are referred to a new orthogonal set of axes,  $X', Y', Z'$ , which affects only the  $B_{1g}$  and  $B_{2g}$  modes. So, their Raman tensors are trans-

formed in such a way that both of these symmetry modes are observed together.

Because of the lack of polarization, the symmetry assignment was not obvious and we have to consider the relative intensity of each line. In particular, the three lines at 127, 597, and 919  $\text{cm}^{-1}$  have comparable intensity for both  $X(YZ)Y$  and  $Z(YY)X$  polarizations (spectra 2 and 3 in Fig. 3); therefore they can be associated with  $B_{1g}$  and  $E_g$  modes. But in view of the results obtained by Syme *et al.* (1), a very weak peak at 129.5  $\text{cm}^{-1}$  and a more intense peak at 126  $\text{cm}^{-1}$  corresponding, respectively, to  $E_g$  and  $B_{1g}$  symmetries, one can assume that in our case the  $E_g$  mode is missing or masked by the 127  $\text{cm}^{-1}$  which presents a half-height width of 2.5  $\text{cm}^{-1}$ . According to the number of each symmetry modes predicted by the group theory, these three lines should be associated with  $B_{1g}$  modes, but a doubt remains for the assignment of the 127- $\text{cm}^{-1}$  line.

### Infrared

The analysis of the IR spectra is simpler than for Raman because only two modes

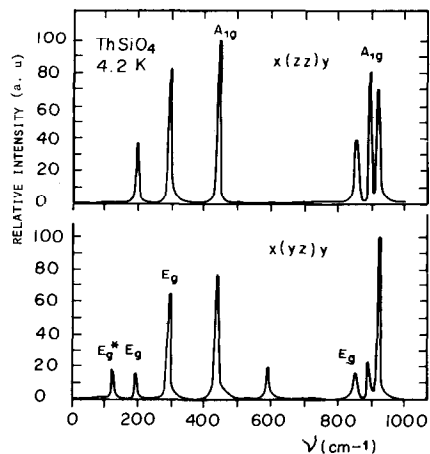


FIG. 4. Raman spectra of thorite recorded at 4.2 K for two adopted geometries:  $X(ZZ)Y$  and  $X(YZ)Y$ . \* The symmetry mode could be  $B_{1g}$ .

TABLE II  
PEAK FREQUENCIES  $\nu$  OF THE ACTIVE RAMAN  
MODES OF THORITE AND THEIR POLARIZATIONS<sup>a</sup>

$\nu$ (cm <sup>-1</sup> )		Polarization 300 K	Symmetry
300 K	4.2 K		
127	126.5	(XZ), (YZ), and (YY)	B <sub>1g</sub> or E <sub>g</sub> (e)
194	193	(XZ), (YZ)	E <sub>g</sub> (e)
265		(XY)	B <sub>2g</sub> (i)
294	294.5	(XZ), (YZ)	E <sub>g</sub> (e)
312		(YY)	B <sub>1g</sub> (e)
440	439	(ZZ)	A <sub>1g</sub> (i)
518	abs	(XZ), (YZ)	E <sub>g</sub> (i)
597	595.5	(XZ), (YZ), and (YY)	B <sub>1g</sub> (i)
855	856	(XZ), (YZ)	E <sub>g</sub> (i)
893	894	(ZZ)	A <sub>1g</sub> (i)
919	921	(XZ), (YZ), and (YY)	B <sub>1g</sub> (i)

<sup>a</sup> The distinction between internal and external modes is denoted by (i) and (e).

are allowed by the selection rules: E<sub>u</sub> and A<sub>2u</sub> (see Theoretical Considerations).

The spectra recorded at room temperature for various wavenumber regions are represented in Fig. 5.

Because of the isomorphism between the structure of zircon and thorite, one can assume that the normal modes are the same in both crystals. Then the shift in frequency for each vibration is only due to the difference between the zirconium and the thorium masses. Therefore, in the absence of polarized spectra for thorite, the mode symmetries (Table III) were determined by correlation between our observed frequencies and those obtained by Dawson *et al.* (2) on the polarized infrared spectra of zircon.

### General Remarks

For both infrared and Raman spectra the assignment of the internal modes was done on the basis of the free silicate measurements reported in the literature (12, 13) for a *T<sub>d</sub>* symmetry group (Fig. 6). Rotatory and translatory labels for the external modes are derived from Dawson *et al.* (2).

The internal frequencies (except the B<sub>2g</sub>

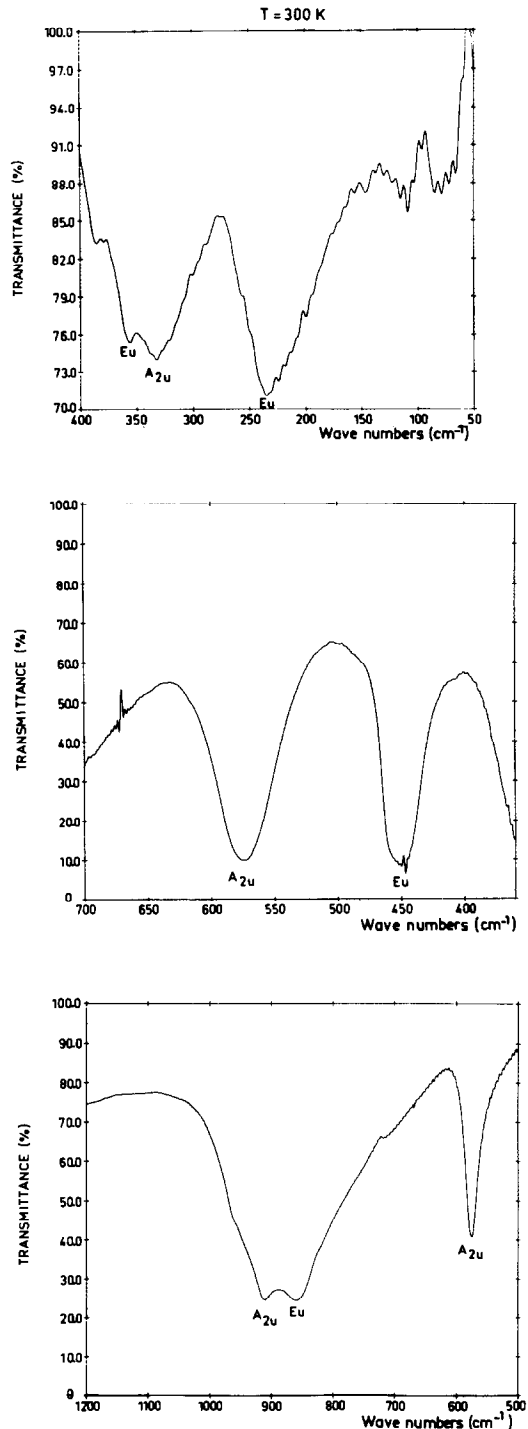


FIG. 5. Unpolarized infrared spectra of thorite recorded at room temperature.

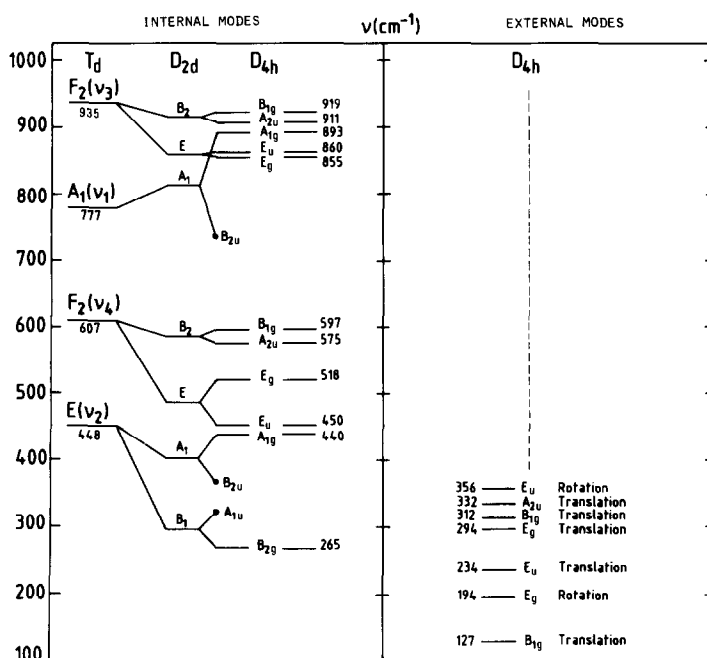


FIG. 6. On the left side: Correlation diagram between the  $\text{SiO}_4^{4-}$  free ion vibrations in the  $T_d$  symmetry (12) and the  $\text{ThSiO}_4$  lattice internal vibrations in the  $D_{4h}$  symmetry (where two units of  $\text{SiO}_4$  are involved), via the  $D_{2d}$  symmetry of one  $\text{SiO}_4$  in the crystal. On the right side: The external modes.

mode at  $265 \text{ cm}^{-1}$ ) are higher in energy than the external ones, owing to the different masses engaged in each class, respectively Si and Th. However, a comparative study with the zircon frequencies points out that

TABLE III

FREQUENCIES  $\nu$  OF THE SEVEN ACTIVE INFRARED MODES OF THORITE AND THEIR ASSIGNMENT DEDUCED FROM THE POLARIZED INFRARED STUDY OF ZIRCON (2) ISOMORPHOUS WITH THORITE

ZrSiO <sub>4</sub> 300 K	ThSiO <sub>4</sub> 300 K	Symmetry
287	234	E <sub>u</sub> (e)
338	332	A <sub>2u</sub> (e)
389.5	356	E <sub>u</sub> (e)
430.5	450	E <sub>u</sub> (i)
608	575	A <sub>2u</sub> (i)
885	860	E <sub>u</sub> (i)
989	911	A <sub>2u</sub> (i)

the distinction between internal and external modes is not obvious. Indeed, a slight decrease of frequency from zircon to thorite for the internal motions, shows that the involved stretching vibration (Si–O) depends on the lattice environment through the influence of the oxygen-cation ( $\text{Th}^{4+}$  or  $\text{Zr}^{4+}$ ) force constant and unit cell volume (3). Moreover the mass effect between Th and Zr cannot explain alone the shift in frequency for the external modes. Then we have to consider that the mixing between modes of a same symmetry can modified the type of vibration given by the theoretical model.

## Conclusion

The work related in this paper led us to determine all the vibration frequencies of thorite  $\text{ThSiO}_4$  (except one Raman mode) and their symmetry in the  $D_{4h}$  factor group.

In addition, the low-temperature experiments in Raman scattering led to the conclusion that the crystal structure of ThSiO<sub>4</sub> remains the same in the temperature range of 300 to 4.2 K.

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