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Journal of Solid State Chemistry 173 (2003) 54–58

JOURNAL OF SOLID STATE CHEMISTRY

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Raman spectroscopy of arsenolite: crystalline cubic As_4O_6

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Received 25 September 2002; received in revised form 20 December 2002; accepted 10 January 2003

Abstract

The complete Raman spectrum of arsenolite, cubic crystalline As_4O_6, is reported for the first time. The previously unseen E_g mode has been found at 443 cm^{-1}. Further, there is additional support for the assignment of the 415 cm^{-1} mode as T_{2g}.

Keywords: Raman; Arsenolite; As_2O_3; As_4O_6; Claudetite; Adamantanoid

1. Introduction

The group V oxides comprise a varied and diverse set of inorganic chemistry. Of particular interest are those compounds which form adamantanoid cages (X_4Y_{6-10}; X=P, As, Sb; Y=O, S) [1–3]. Interest in these compounds has been significant due in part to their suitability as general models for solid-state systems [4,5] and in a wide variety of industrial applications. For instance, P_4O_{10} is being used in the development of high-energy laser glasses [6] as well as in the vitrification of spent nuclear wastes [7]. Another group V oxide, As_2O_3, has also received considerable interest for many reasons. Among them are its formation of deleterious microcrystalline impurities during the fabrication of semiconductors such as GaAs [8], its uses as a pesticide, and the similarity in structure to an emerging class of chemical warfare agents. Additionally, As_2O_3 has shown promise in treating solid tumors associated with acute promyelocytic leukemia [9].

As such, the electronic structure and vibrational characteristics of As_4O_6 in its vapor and solid forms are of interest. Arsenic oxide in the gas phase has been shown [10] to exist as As_4O_6, a spherical-top dimer with T_d symmetry. Measurements of its IR [11,12] and Raman [10,13,14] spectra have been previously reported with some ambiguities in the assignments. Specifically, the ambiguities involve two T_2 vibrations and one unobserved E.

The solid forms of As_4O_6 include vitreous, claudetite I, claudetite II, and arsenolite. According to Grzechnik [15], the structure of the vitreous form is somewhat unclear at this time due to conflicting experimental evidence. The claudetite forms are monoclinic, assuming a “puckered-layer” structure, and are very similar to orpiment (As_2S_3).

The last solid form, arsenolite, is the focus of this research effort. It is the cubic crystalline phase of As_4O_6. Ballirano and Maras [16] have recently completed a powder refinement of the structure with the following parameters: $Fd3m$ (No. 227) space group, $a = 11.07343(5)$ Å, $V = 1357.8$ Å^3, $Z = 16$, $R(P) = 0.056$, $wR(P) = 0.073$, $R(I) = 0.068$, and $T = 295$ K. The As–O bond distance is 1.786(2) Å, and the O–As–O and As–O–As bond angles are 98.4(2)° and 128.7(3)°, respectively. The primitive unit cell contains two As_4O_6 adamantanoid molecules (As_2O_3 “dimers”, see Fig. 1) situated on the T_d sites of the unit cell [13,17].

Factor group analysis of an isolated As_4O_6 molecule in T_d symmetry gives

$$\Gamma_{\text{vib}} = 2A_1 + 2E + 2T_1 + 4T_2$$

for the irreducible representation of the vibrational modes. Treating the As_4O_6 units in arsenolite as discrete molecules (intermolecular O–O distance is 0.3022 nm)

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doi:10.1016/S0022-4596(03)00082-3

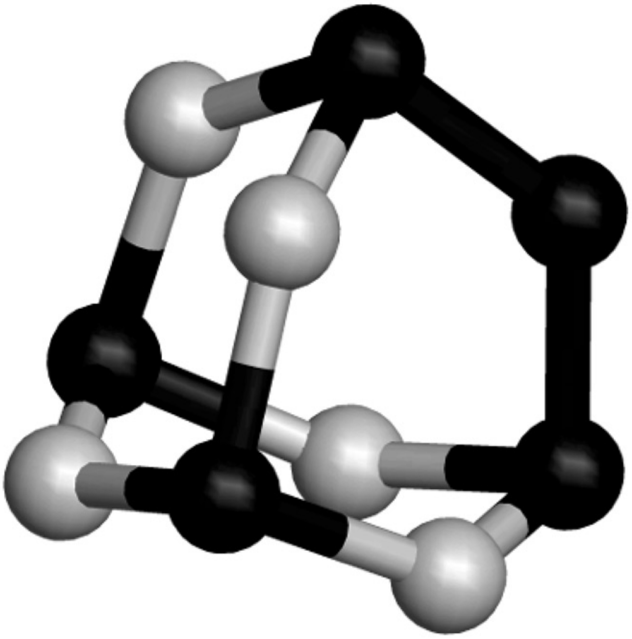

Fig. 1. Molecular modeling representation of As_4O_6 found in arsenolite. The light gray spheres represent the As atoms and the dark gray spheres the O atoms.

gives

$$\Gamma_{\text{int}} = 2A_{1g} + 2E_g + 2T_{1g} + 4T_{2g} + 2A_{1u} + 2E_u + 2T_{1u} + 4T_{2u}$$

for the internal representation [16,18]. The A_{1g}, E_g and T_{2g} are Raman active while the T_{1u} modes are IR active.

To date, several studies have been published on arsenolite's Raman and IR spectra [13–15,19]. However, similar to the gas-phase case, there remains one E_g vibrational mode yet to be observed, and some disagreement on the assignment of T_{2g} and E_g modes. To clarify this issue, the complete Raman spectra of a sample of arsenolite was collected and analyzed.

2. Experimental

As_4O_6 was purchased from Alfa-Aesar (purity 99.999% metals basis). X-ray powder diffraction was used to check for phase purity. The diffraction pattern was recorded using a Scintag (now Thermo Arl) XDS-2000 diffractometer with a liquid-nitrogen-cooled solid-state germanium detector (EG&G Ortec, model GLP-L0195107-S) and a Cu$K\alpha$ radiation (45 kV, 40 mA) source. For this experiment, a Bragg–Brentano $\theta - \theta$ setup was used with an angular range of 60°, step size of 0.03°, and a counting time of 0.45 s/°.

Samples for Raman spectroscopy were sealed in glass capillaries under a dry nitrogen (BOC gas, 99.990%) atmosphere. The spectrometer was a SPEX model 1403 double monochromator with 0.85 m pathlengths and 1800 g/mm gratings. The monochromator's exit slit was removed and a Princeton Instruments model NTE CCD array detector installed. This array is approximately 27 mm wide with 1340 × 100 pixels. Given the linear dispersion of the monochromator, each spectral segment or "window" was approximately 200 cm^{-1} wide.

The excitation source consisted of a Coherent Inova 90-5 Argon Ion CW laser emitting at 514.5 nm with an output power of 1.6 W. This output was transmitted through an SPEX plasma filter to remove the unwanted emission lines. Additionally, a Kaiser Optical Systems Holographic Super Notch-Plus Filter (part number HSPF-514.5-2.0) was used to reduce the intensity of the resonant laser scatter from the sample.

The entrance slit to the monochromator was set at 50 μm. The integration time for the CCD array was 1.0 s with 20 scans coadded to form the final spectrum. The Raman shifts were calibrated using the ASTM E-1840 standard values for naphthalene [20]. The resolution of the collected spectra was less than 0.5 cm^{-1} with a reproducibility of $< 1.0\,cm^{-1}$.

3. Results and discussion

3.1. X-ray diffraction

The powder X-ray diffraction pattern for the As_4O_6 sample is shown in Fig. 2. The sample has excellent crystallinity, with a FWHM of 0.14° 2θ. There is no evidence of significant claudetite I or claudetite II impurities as shown by the absence of the 3.454 Å diffraction peak at 12.90°, and is therefore considered to be phase-pure arsenolite.

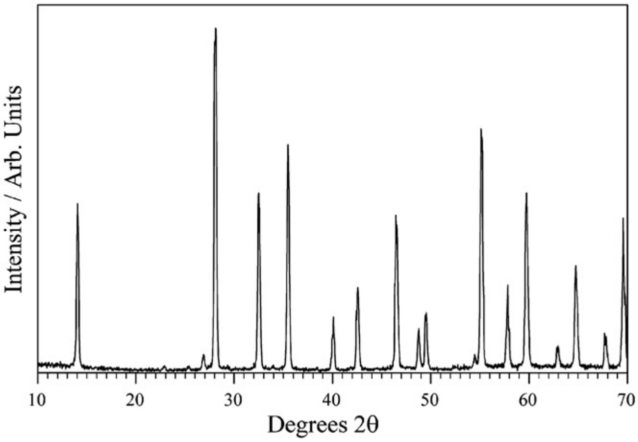

Fig. 2. Powder X-ray diffraction pattern for the As_4O_6 sample used in this work. The sample has excellent crystallinity and is phase-pure arsenolite with no evidence of claudetite I, claudetite II, or an amorphous phase.

3.2. Raman spectrum

The Raman spectrum was collected as a series of discrete overlapping segments rather than as a continuous scan using the CCD array. The resulting spectrum of the As_4O_6 sample is given in Fig. 3. There were 18 distinct peaks observed. These along with their assignments and relative intensities are given in Table 1.

For the most part, this spectrum is in agreement with Beattie et al. [13] and Grzechnik [15]. The intense A_{1g} modes may be found at 370 and 561 cm^{-1}. There is an E_g mode at 184 cm^{-1} and three of the four T_{2g} modes may be found at 268, 472, and 781 cm^{-1}.

Previously unreported are several peaks consistent with combination bands. The peaks at 536 and 828 cm^{-1} are second harmonics of the T_{2g} mode at 268 cm^{-1} and the peak at 415 cm^{-1}, respectively. The peak at 828 cm^{-1} can also be explained through the addition of an A_{1g} mode (561) and a T_{2g} mode (268) to form a summation band. The peaks at 228 (415–184), 327 (415–89), 511 (781–268), and 598 (781–184) cm^{-1} are consistent with difference bands. The peaks at 598 and 1049 cm^{-1} may also be explained as (184 + 415) and (781 + 268) summation bands, respectively.

Grzechnik assigns the peak observed at 89 cm^{-1} as T_{2g} belonging to a translational mode of the As_4O_6 molecule in the crystal. One would expect the translational modes of the molecule to occur at low wave numbers, and since this mode is not observed in the gas phase spectrum [13,15], this is a reasonable explanation.

This leaves three peaks in the spectrum unexplained, namely 415, 443, and 760 cm^{-1}. No simple harmonic or combination mode explanation is available for these three peaks. The 760 cm^{-1} peak, on the shoulder of the T_{2g} (781), has a very small relative intensity of 0.06 and does not correspond to a mode observed for claudetite I, claudetite II or the vitreous phases in As_4O_6 [19,21–24]. It has been left unassigned and may simply be a perturbation of the T_{2g}.

Grzechnik labels the peak at 415 cm^{-1} as T_{2g} based on pressure-dependence data [15], while Lucovsky et al. designate this peak as an E mode [19]. In Beattie et al. [13] this peak was too weak to assign. Qualitative peak shape arguments suggest that it is a fundamental mode and not a harmonic or combination band (see Fig. 3). The regular gaussian line shape is comparable to the other T_{2g} modes and is unlike the broader and more irregular line shapes of the combination bands. This qualitative argument would limit the assignment to the as yet unaccounted for T_{2g} and E_g modes. Without evidence to the contrary, and given that Lucvosky et al. question their own assignment, the most reasonable explanation is that this is the T_{2g} mode.

Sourisseau and Mercier estimate the unobserved E band at 470 cm^{-1} based on the results for vitreous As_4O_6 [25]. Recent ab initio vibrational calculations (J.O. Jensen et al., unpublished results; S.J. Kirkby, unpublished results) for the isolated As_4O_6 molecule indicate that the unobserved E mode is between the two A_{1g} modes. This suggests that the missing E_g mode should

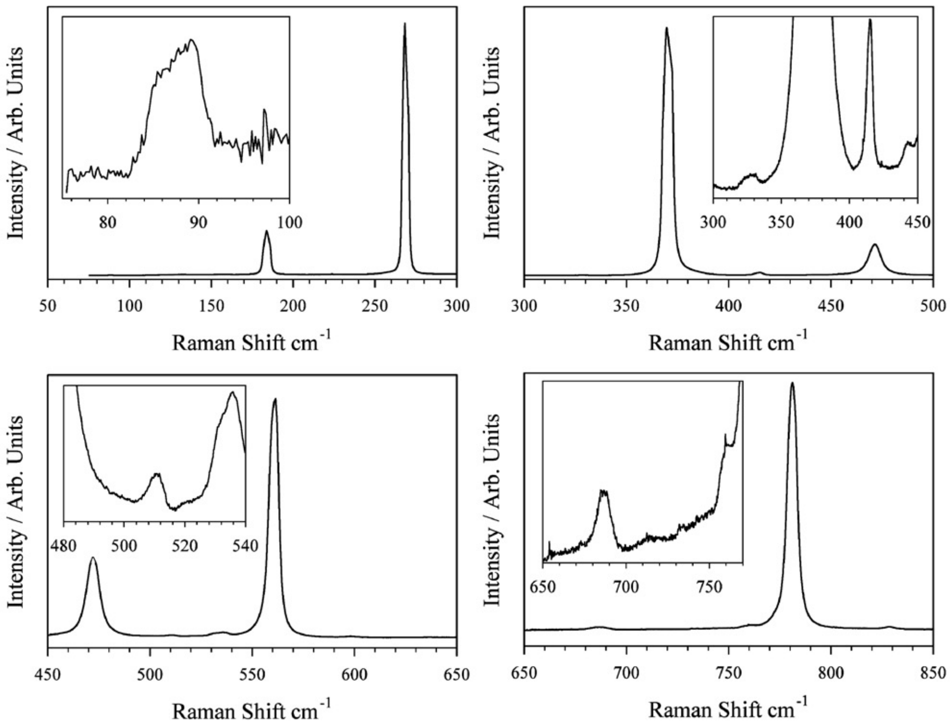

Fig. 3. Raman spectrum of As_4O_6. The peak locations, relative intensities, and assignments are given in Table 1.

Table 1
Peak assignments for the Raman spectrum of arsenolite, cubic crystalline As_4O_6 (values from previous studies are included for comparison)

Peak	Assignment	Observed (cm−1)	Relative intensity	Beattie et al. [13]	Brumbach and Rosenblatt [14]	Grzechnik [15]	Lucovsky and Galeener [19]
1	T_{2g} (trans. mode)	89	0.08	86vs	85	82	
2	E_g	184	14	184w	189	182	185
3	[7]–[2]	228	1.1				
4	T_{2g}	268	79	268s	269	266	253,346
5	[7]–[1]	327	0.07				
6	A_{1g}	370	100	370s	371	368	381
7	T_{2g}	415	0.95	417vw	416	413 (T_{2g})	409 (E)
8	E_g	443	0.06				
9	T_{2g}	472	12	470w	470	469	496
10	[16]–[4]	511	0.15				
11	2 * [4]	536	0.35				
12	A_{1g}	561	33	560s	560	559	556
13	[2] + [7]						
	[16]–[2]	598	0.13				
14	[4] + [7]	687	0.13				
15	Unidentified	760	0.06				
16	T_{2g}	781	13	780w	782	780	782
17	2 * [7]						
	[7] + [4]	828	0.11				
18	[16] + [4]	1049	0.04				

Note: In the assignment column, the [x] notation is used to designate peak number x for harmonics and combination bands.

be found in the range between the two A_{1g} modes, that is, 370–561 cm^{-1}. The only observed peak in this region as yet unassigned is the one at 443 cm^{-1}. Thus, by this process of elimination, the peak at 443 cm^{-1} is assigned to the E_g mode.

One possible reason the E mode at 443 cm^{-1} has been difficult to see in the past is its especially small relative intensity (0.06) compared to other modes in the spectrum. An additional dilemma is that the mode occurs in the wing of the rather large T_{2g} mode (472) and may be obscured by the broader T_2 peak in the gas-phase spectrum (cf. [13]).

4. Summary

The complete Raman spectrum for arsenolite has been recorded for the first time. The previously unobserved E_g mode has been found at 443 cm^{-1}. Completion of the vibrational spectrum will assist in the understanding of the ground state of As_4O_6 and the electronic structure of arsenolite.

Acknowledgments

The authors express their gratitude for the funding provided by the US Army's Edgewood Chemical and Biological Center. The authors thank the Materials Research Center at the University of Missouri-Rolla for the use of their X-ray powder diffractometer.

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