

Brief Reports

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Raman scattering from VO₂ single crystals: A study of the effects of surface oxidation

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VO₂ single crystals were studied in an effort to resolve the differences that are present in two previous reports on the Raman spectra of VO₂. We find that surface oxidation effects that change the stoichiometry of the material at the surface layer produce large shifting of the Raman spectral peaks. The experimental evidence is presented and the relation to the previous Raman studies of VO₂ are discussed.

Vanadium dioxide has drawn most of its attention due to the material's metal-insulator transition (MIT) that occurs above room temperature at 68 °C.¹ The MIT produces a change in the crystal structure from the low-temperature monoclinic phase to the high-temperature tetragonal phase. In conjunction with the structural modification is a change in the optical² and transport³ properties (as large as 5 orders of magnitude in the resistivity).

Raman scattering has been used as a probe to understand the electron-phonon interactions of VO₂ since it is believed that these interactions are an important mechanism in the MIT.^{4,5} Two independent groups performed Raman measurements on VO₂ single crystals at temperatures above and below the MIT. Both groups showed a very strong change in the Raman spectrum brought on by the MIT; however, the two interpretations of the results were quite different. The most striking feature of these studies were the obvious differences in the spectra of the two groups, primarily in the spectral peak positions and mode symmetry assignments. These spectral differences have never been resolved and still remain a mystery. In this brief report, we present a series of Raman measurements done on VO₂ single crystals grown in our laboratory. We will demonstrate the probable mechanism that is responsible for the differences in the previously reported Raman spectra of VO₂ and determine the correct Raman signature for VO₂.

The VO₂ single crystals fabricated for this study were grown in our laboratory by a previously prescribed method.⁶ The samples were analyzed by x-ray diffraction in order to establish that the crystal's lattice constants were that of VO₂.⁷ Resistivity measurements in the temperature range of 20–100 °C showed a sharp MIT at

68 °C with a width of about 2 °C, indicative of stoichiometric VO₂.⁶ The Raman measurements were carried out using a Jobin-Yvon Optical System U-1000 double-grating spectrometer and a Coherent, Inc. Ar⁺ ion laser operating at 5145 Å. The details of the system have been outlined previously.⁸ All of our measurements were done with the spectrometer slits set for a 1-cm⁻¹ resolution. The laser power was kept below 100 mW to prevent any sample heating, and from an analysis of the Stokes–anti-Stokes ratio we determined that the laser increased the sample temperature 2–4 °C.

Figure 1(a) shows the room-temperature Raman spectrum obtained from the cleaved face of one of our single-crystal samples. The spectrum was measured in a back-scattering geometry with the incident and scattered light polarized along the monoclinic *c* axis. As can be seen the spectrum is dominated by two sharp peaks at 191 and 223 cm⁻¹ and a broader peak at 613 cm⁻¹. The weaker peaks are identified in Table I. All the modes were found to have A_g symmetry except for the peak at 142 cm⁻¹ whose symmetry we could not identify. The spectral features, peak positions, and mode symmetry assignments agree quite favorably with the results of Aronov *et al.*⁵ with the peak positions listed for comparison in Table I. At temperatures above the MIT we found no identifiable peaks or structure in the spectrum which also agrees with the results of Aronov *et al.*

These Raman measurements are quite different⁹ from those obtained by Srivastava and Chase.⁴ Table I shows the peak positions determined from the room-temperature Raman measurements of Srivastava and Chase,⁴ and as can be seen the differences in peak position are far beyond reasonable experimental error.⁹ The mode-symmetry assignments made by Srivastava and

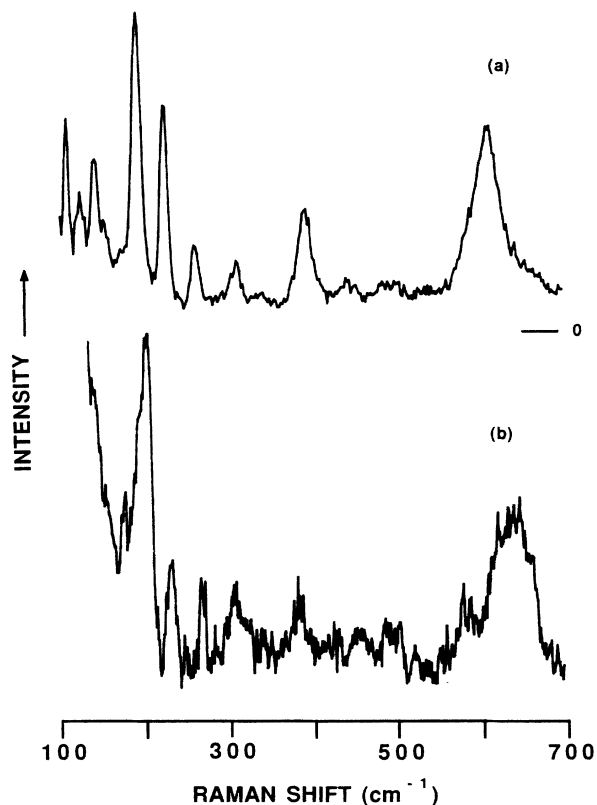


FIG. 1. The Raman spectra of VO_2 single crystals that are (a) stoichiometric and (b) oxygen rich. The oxygen-rich material was made by allowing a stoichiometric sample to age for 15 months in air or rapidly oxidized by annealing a stoichiometric sample in air at 400°C .

Chase were derived from a reduction of the rutile mode symmetries. The results of Srivastava and Chase also show that the Raman spectrum measured at temperatures above the MIT has a very broad peak near 500 cm^{-1} . This result is quite different from our measurements which show no structure in the Raman spectrum, whatsoever.

Recent experiments have shown that the Raman spectrum of an oxide material can be greatly effected by deviations in oxygen stoichiometry.^{8,10} It is quite apparent that the results presented here and those of Aronov *et al.* are substantially different from the results of Chase and Srivastava and perhaps the differences may be attributed to an oxygen deficiency or richness in the VO_2 crystals. The x-ray and resistivity measurements performed on our VO_2 single crystals indicate that the samples are stoichiometric VO_2 ; therefore, we can conclude that the spectrum obtained in this work would be the identifiable spectrum of stoichiometric VO_2 .

The role that oxygen might play in altering the stoichiometry of VO_2 would be as follows. The most stable oxygen composition¹¹ of vanadium oxide is V_2O_5 which obviously has a larger $[\text{O}]/[\text{V}]$ ratio than VO_2 . Therefore, one would expect that the natural aging of VO_2 would be an absorption of oxygen from the atmo-

TABLE I. Comparison of Raman peak positions measured in this work and the results of previous studies. The data in the columns labeled stoichiometric and oxygen rich are the spectral peak positions determined from Figs. 1(a) and 1(b), respectively. The data in the inner columns are previous results of Aronov *et al.* (Ref. 5) and Srivastava and Chase (Ref. 4). All data units are cm^{-1} .

Stoichiometric	Ref. 5	Ref. 4	Oxygen rich
142	142		
191	191	208	202
223	222	236	232
262	259		266
310	308		305
	335		382
392	389		
443		450	455
500	497		504
613	611	655	580
		850	640

sphere which would drive the material toward the composition V_2O_5 . This natural progression of adjusting the materials stoichiometry could have strong implications on the Raman spectrum if it is sensitive to these changes.

We have performed two test experiments on our VO_2 single crystals in order to confirm this hypothesis. The first experiment was to let a freshly cleaved VO_2 crystal naturally age in a humid atmosphere for a long period of time. To achieve this we let one of our samples age in air with an average humidity of about 70% for a period of 15 months. The second technique was to produce a more rapid oxidation of one of our samples by annealing it at 400°C for 1 h in air. We did not expect either condition would produce a uniform volume oxidation of our samples; more likely, the largest effects of a natural or rapid oxidation would reside in the surface layer. This was not a problem for us since our measurements were only capable of probing the surface layer of the samples due to the small beam penetration depth which we calculated to be about 1500 \AA .

The result of the oxidation experiment is presented in Fig. 1(b) which shows the room temperature Raman spectrum obtained from the sample that naturally aged for 15 months in air. As can be seen the spectrum is quite different from that obtained from the stoichiometric VO_2 sample. The apparent trend of the oxidation is to shift the major spectral peaks at 191 , 223 , and 613 cm^{-1} to higher frequencies of 202 , 232 , and 640 cm^{-1} , respectively. It is of interest to note that the peak positions (shown in Table I) are quite similar to the room-temperature results of Srivastava and Chase. To confirm that this was a surface oxidation effect, we recleaved our oxidized sample and examined the inner portion and found that we were in fact able to reproduce the spectrum shown in Fig. 1(a). Similar results were seen for the sample that was annealed at 400°C in air. This sample also showed a shifting of the major spectral peaks to higher frequencies, clearly indicating that the spectral changes were due to a surface oxidation effect. The mode

symmetries of these samples were not determined.

In summary, we have established a Raman signature for stoichiometric VO_2 and demonstrated the effect that the oxygen stoichiometry has on the Raman measurements of this material. From these results we suggest that stoichiometry effects may have been an important contribution to the differences that were seen in the previously reported Raman spectra of VO_2 .

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