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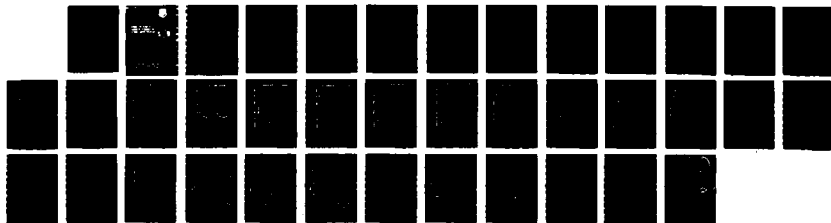
RAMAN SCATTERING AS A DIAGNOSTIC TECHNIQUE FOR CATHODE  
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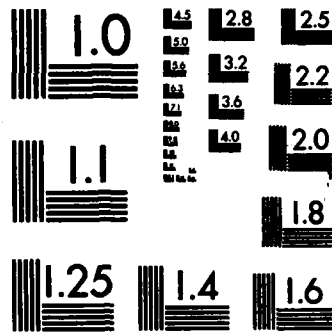
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**Final Technical Report**  
**June 1987**



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**RAMAN SCATTERING AS A  
DIAGNOSTIC TECHNIQUE FOR  
CATHODE CHARACTERIZATION**

**University of Utah**

**Robert E. Benner, J. R. Mitchell and R. W. Grow**

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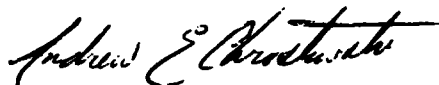
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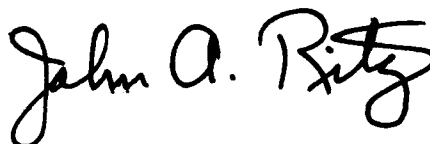
ANDREW E. CHROSTOWSKI, 1Lt, USAF  
Project Engineer

APPROVED:



FRANK J. REHM  
Technical Director  
Directorate of Surveillance

FOR THE COMMANDER:



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<p>The feasibility of using the optical technique of Raman scattering to determine the chemical composition of cathode surfaces has been investigated. Reference Raman spectra have been obtained for many of the chemical compounds expected to be present at the surface of dispenser cathodes. In addition, spectra obtained from 5-3-2 impregnant and several cathode surfaces are presented. The potential advantages of the approach are discussed.</p>				
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TABLE OF CONTENTS

	<u>Page</u>
LIST OF ILLUSTRATIONS AND TABLES . . . . .	v
I. INTRODUCTION . . . . .	1
II. RAMAN SCATTERING . . . . .	2
III. REFERENCE STANDARDS . . . . .	4
IV. CATHODE SPECTRA . . . . .	19
V. DISCUSSION . . . . .	26



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LIST OF ILLUSTRATIONS AND TABLES

<u>Figure</u>		<u>Page</u>
1	Raman spectrum of barium oxide . . . . .	6
2	Raman spectrum of barium tungstate . . . . .	7
3	Raman spectrum of calcium tungstate . . . . .	8
4	Raman spectrum of calcium oxide . . . . .	9
5	Raman spectrum of tungsten oxide WO <sub>2</sub> . . . . .	10
6	Raman spectrum of aluminum tungstate . . . . .	11
7	Raman spectrum of α-Al <sub>2</sub> O <sub>3</sub> . . . . .	12
8	Raman spectrum of tungsten oxide WO <sub>3</sub> . . . . .	13
9	Raman spectrum of calcium carbonate . . . . .	14
10	Raman spectrum of barium carbonate . . . . .	15
11	Raman spectrum of 5-3-2 impregnant powder . . . . .	16
12	Raman spectra of various barium compounds having unique spectral signatures . . . . .	17
13	Raman spectra of various tungstates having unique spectral signatures . . . . .	18
14	Raman spectrum of 5-3-2 impregnant compared with spectra of its nominal constituents . . . . .	21
15	Raman spectra of γ- and α-Al <sub>2</sub> O <sub>3</sub> . . . . .	22
16	Raman spectra from the surfaces of 5-3-2 and 4-1-1 cathodes compared to spectrum of 5-3-2 impregnant powder . . . . .	23
17	Raman spectrum from the surface of 5-3-2 cathode compared with the spectra of selected reference materials . . . . .	24
18	Raman spectra from different portions of the 5-3-2 cathode surface . . . . .	25
19	Calculated blackbody radiation profiles as a function of wavelength for temperatures of 1000 K and 1500 K . . .	27



Figure

Page

20    Calculated blackbody radiation profiles as a function  
of temperatures for wavelengths of 400 nm and 500 nm . . .    28

Table

1    Measured frequency shifts and relative scattering  
intensities for major Raman peaks of pure reference  
materials . . . . .    5

## I. INTRODUCTION

Attempts to improve the performance and extend the operating life of dispenser cathodes have been hindered by an inadequate knowledge of the chemistry which occurs at cathode surfaces during preparation and operation. Because of the chemical complexity of modern cathode structures, this problem is especially acute. If better diagnostic techniques were available to monitor the time evolution of the chemical compounds present at the cathode surface on a microscopic scale during operation, guidelines might be developed for manufacturing improved cathode structures. Furthermore, since the chemical mechanisms of degradation could be probed directly, methods might be found for extending the operational lifetime of cathodes. In this report we present the results of preliminary studies to determine the feasibility of using the optical technique of Raman scattering to determine the chemical composition of cathode surfaces. Potential advantages of the approach include the capability of making in-situ measurements at elevated temperatures, chemical compound identification rather than simple elemental analysis, relatively high (2 micrometer) spatial resolution, and adequate sensitivity for time-resolved measurements of chemical composition on a time scale of seconds. In our studies Raman spectra have been obtained from pure reference powders expected to be present at cathode surfaces, from a 5-3-2 impregnant mixture, and from 5-3-2 and 4-1-1 cathodes.

## II. RAMAN SCATTERING

The Raman scattering technique relies on the interaction of incident monochromatic light with the vibrational modes (phonons) of a scatterer to produce scattered light which is shifted in frequency from that of the incident light by an amount corresponding to the vibrational frequencies of the scatterer. Raman spectra are obtained by measuring the intensity of the scattered light as a function of the frequency shift from the incident light frequency. Peaks in the spectra correspond to excitation of vibrational modes within the scatterer. In general, the vibrational mode frequencies of different chemical compounds are sufficiently unique that the chemical compound constituency of an unknown sample can often be inferred from its Raman spectrum. While the technique is semiquantitative, since the scattered light intensity is proportional to the amount of chemical compound illuminated, the proportionality constants relating scattered light intensity to chemical concentration vary between the various vibrational peaks of individual compounds and from one compound to another. These proportionality constants can be measured by recording individual Raman spectra from pure reference standards.

In our experiments, Raman spectra were recorded using a Raman microprobe system consisting of an argon ion laser, a modified optical microscope, and a triple-grating, scanning spectrometer with a cooled GaAs photomultiplier detector and photon counting electronics. The argon laser operated at a wavelength of 488 nm to produce a beam at a power level of approximately 50-400 mW which was directed through the

objective (40 x) of a conventional optical microscope to produce an illuminated sample area with a diameter of approximately 2 micrometers. Raman scattering from the illuminated spot was collected with the same microscope objective at a numerical aperture of 0.6 and imaged onto the entrance slit of the scanning spectrometer. The incident and scattered light beams were physically separated within the microscope using a dichroic beam splitter. The microscope also included provisions for visual or photographic observation of the illuminated sample area and for translation of the sample relative to the laser beam. A 0.75 m double spectrometer (Spex 1403) with third monochromator attachment was used to analyze the frequency components present in the scattered light. The third monochromator greatly assisted in rejecting diffusely scattered light at the laser wavelength from the detector. Data acquisition including scanning of the spectrometer and accumulation of the Raman scattering signal was accomplished with a personal computer.

### III. REFERENCE STANDARDS

As a first step in evaluating the Raman technique for cathode characterization, reference spectra were obtained from a variety of chemical compounds likely to be present at a cathode surface. All of these reference materials were in powdered form. The measured frequency shifts and relative intensities of some of the major Raman peaks for all of the reference compounds studied are summarized in Table 1. The Raman spectra from which the data of Table 1 were derived are shown in Figs. 1-11. Since all of these spectra were obtained with the same incident light power level, the intensity scales can be compared directly.

Some of the Raman spectra from the reference compounds are compared in Figs. 12 and 13. For clarity of presentation, the intensity scales used in plotting these spectra as well as all of the remaining Raman data in this report are arbitrary and vary from spectrum to spectrum. The zero intensity levels of the spectra are also offset for clarity. Figure 12 illustrates that barium oxide, barium tungstate, and barium carbonate have unique spectral signatures. Consequently, in a mixture of these compounds, each component could be easily identified. Raman spectra from various tungstates are displayed in Fig. 13. Again, unique spectral signatures are observed. In fact, nearly all of the spectra obtained from the various reference standards including other tungstates, carbonates, and oxides of barium, calcium, and aluminum have unique features which would allow each compound to be identified. The Raman spectrum of  $WO_2$  was, however, found to be very similar to that of  $WO_3$ .

Table 1. Measured frequency shifts and relative scattering intensities for major Raman peaks of pure reference materials.

	<u>Frequency Shift (cm<sup>-1</sup>)</u>	<u>Relative Intensity</u>
Barium oxide	127	4.7
BaO	691	0.7
	1056	4.3
Barium tungstate	328	45.7
	791	20.4
BaWO <sub>4</sub>	828	16.4
	922	80.5
Calcium tungstate	115	12.3
CaWO <sub>4</sub>	212	7.4
	330	26.7
	397	8.7
	795	9.7
	839	6.1
	906	73.0
Calcium oxide	108	0.2
CaO	359	0.8
	687	0.2
	1084	0.2
Tungsten oxide	127	0.4
WO <sub>2</sub>	254	0.3
	702	0.2
	802	0.4
Aluminum tungstate	129	0.4
Al <sub>2</sub> (WO <sub>4</sub> ) <sub>3</sub>	347	0.8
	810	1.1
	1030	1.1
Alumina	382	1.3
α-Al <sub>2</sub> O <sub>3</sub>	415	2.1
	575	0.2
	644	0.4
	752	0.5
Tungsten oxide	127	1.5
WO <sub>3</sub>	252	2.1
	710	3.8
	802	7.1
Calcium carbonate	154	2.2
CaCO <sub>3</sub>	281	4.2
	710	1.4
	1088	11.0
Barium carbonate	133	19.3
BaCO <sub>3</sub>	148	14.8
	223	2.6
	693	3.0
	1062	26.1
5-3-2 Impregnant	127	2.3
	692	0.4
	1060	2.2
	1088	1.0

# BARIUM OXIDE

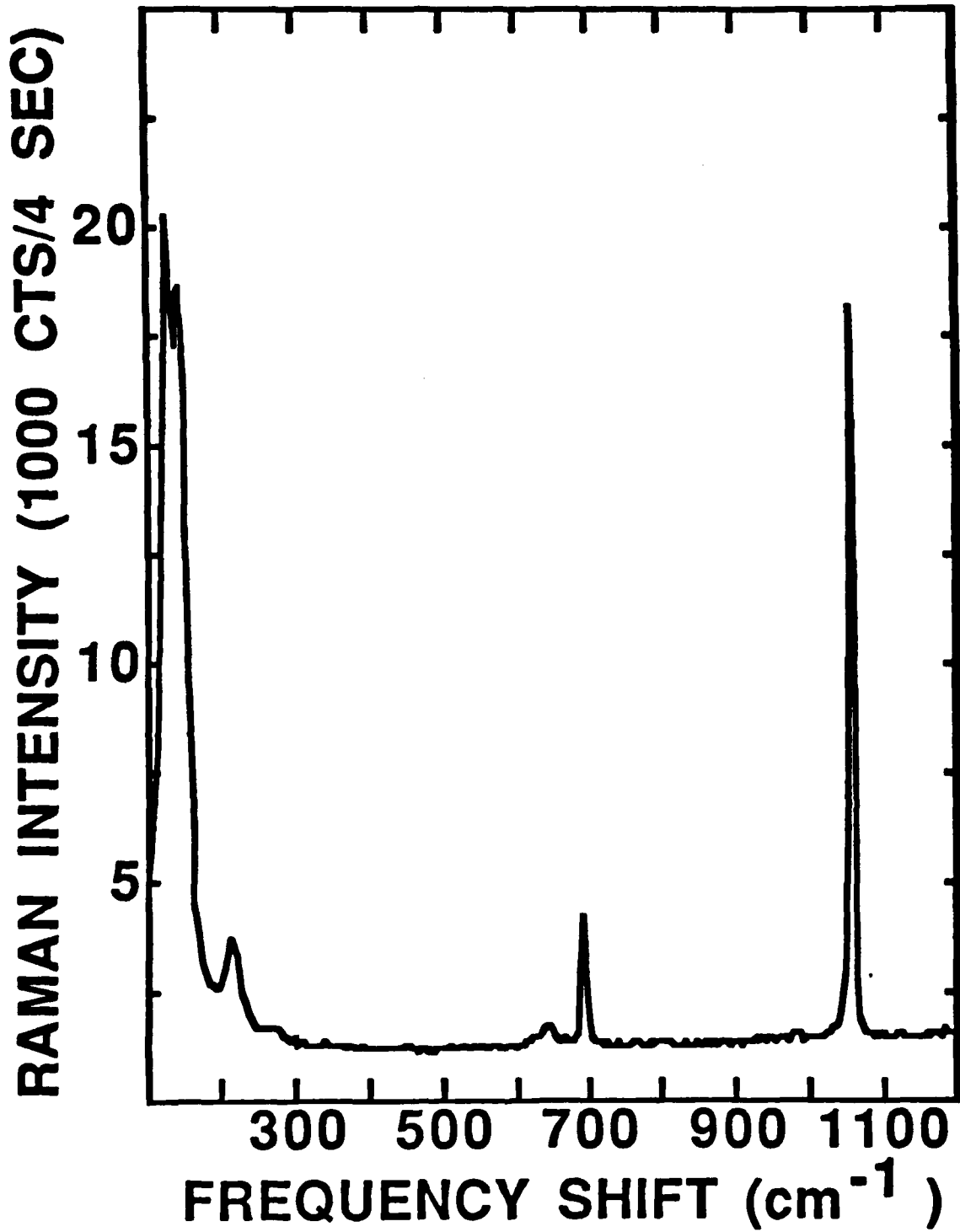


Fig. 1. Raman spectrum of barium oxide.

# BARIUM TUNGSTATE

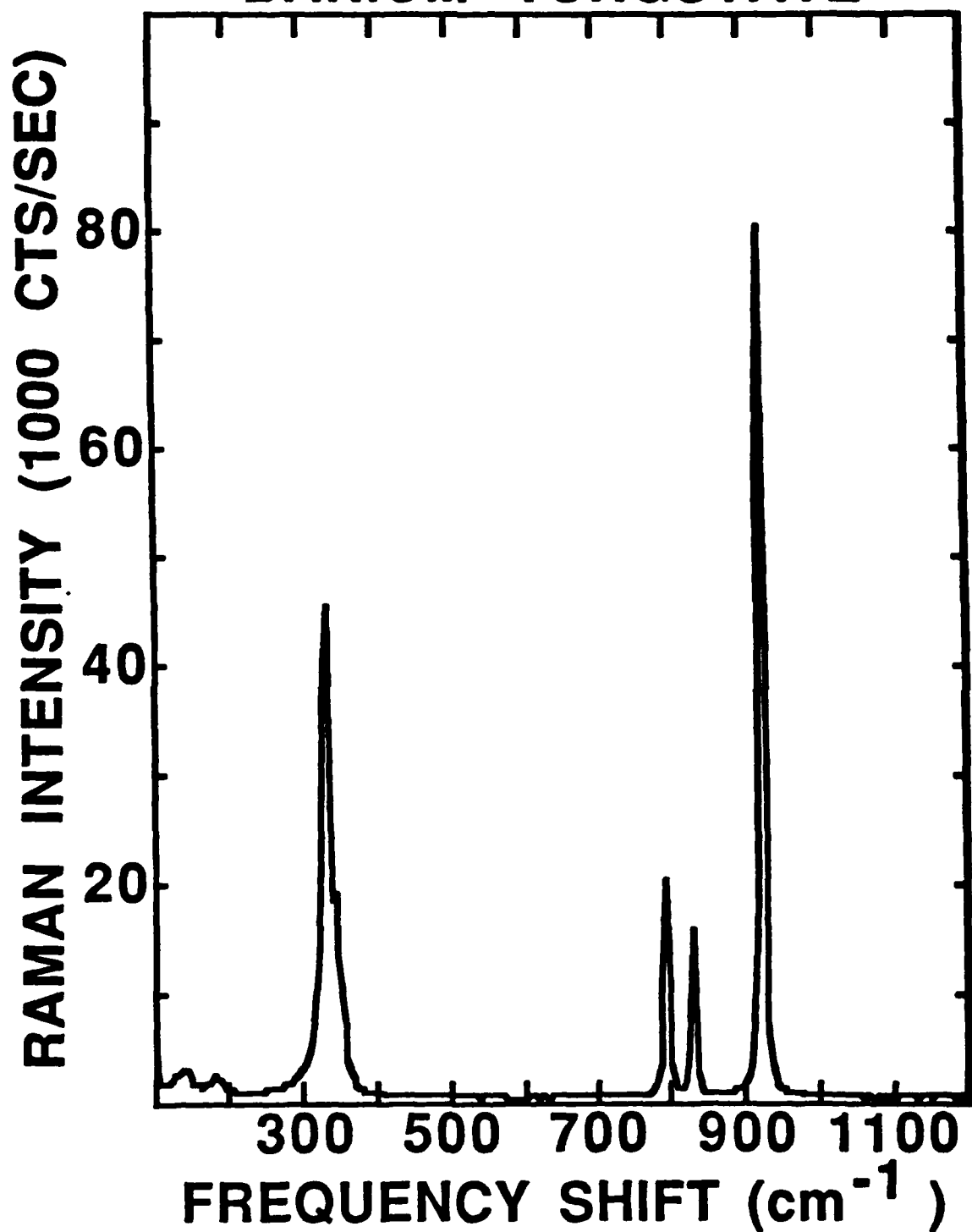


Fig. 2. Raman spectrum of barium tungstate.



# CALCIUM TUNGSTATE

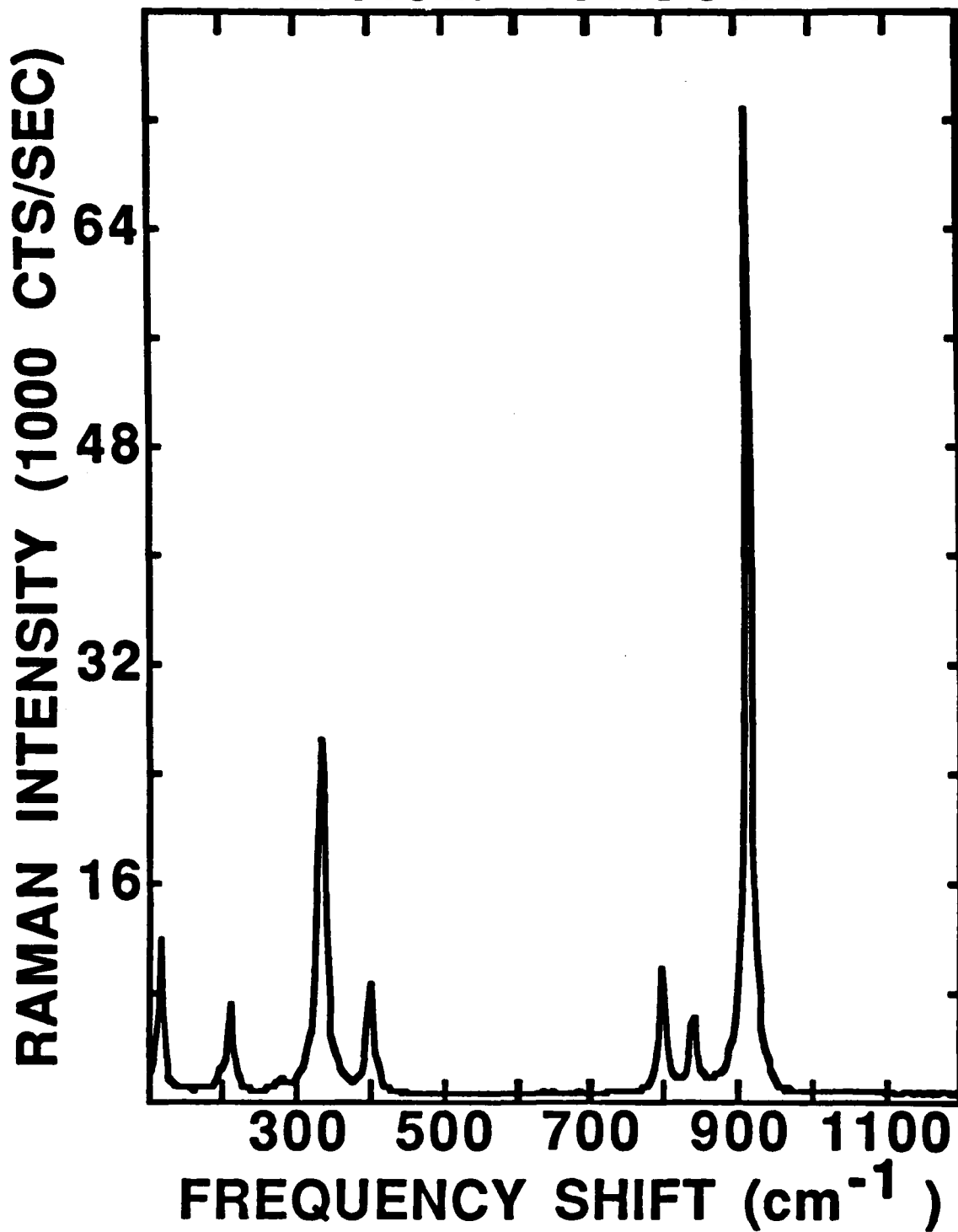


Fig. 3. Raman spectrum of calcium tungstate.

# CALCIUM OXIDE

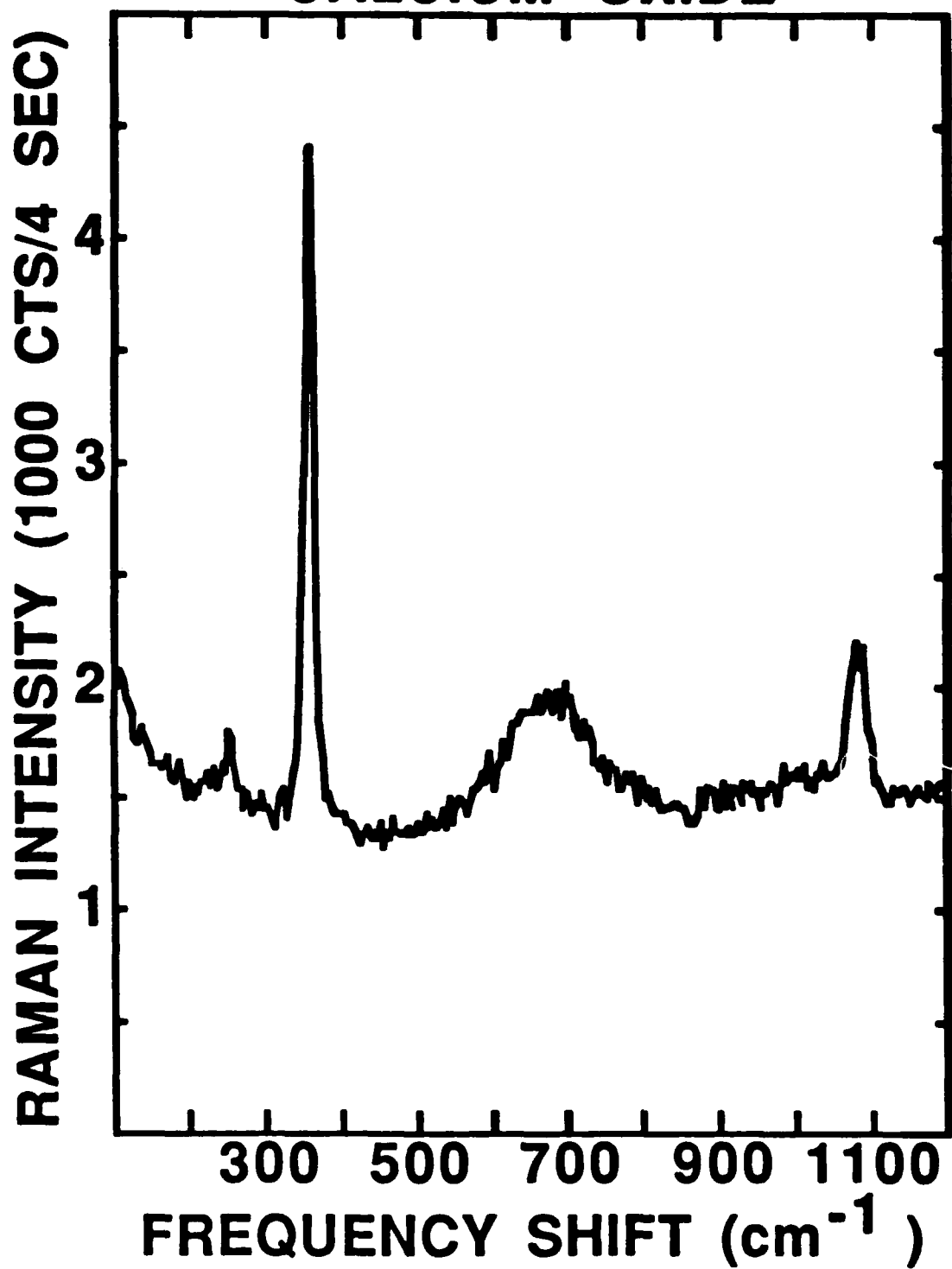


Fig. 4. Raman spectrum of calcium oxide.

# TUNGSTEN (IV) OXIDE

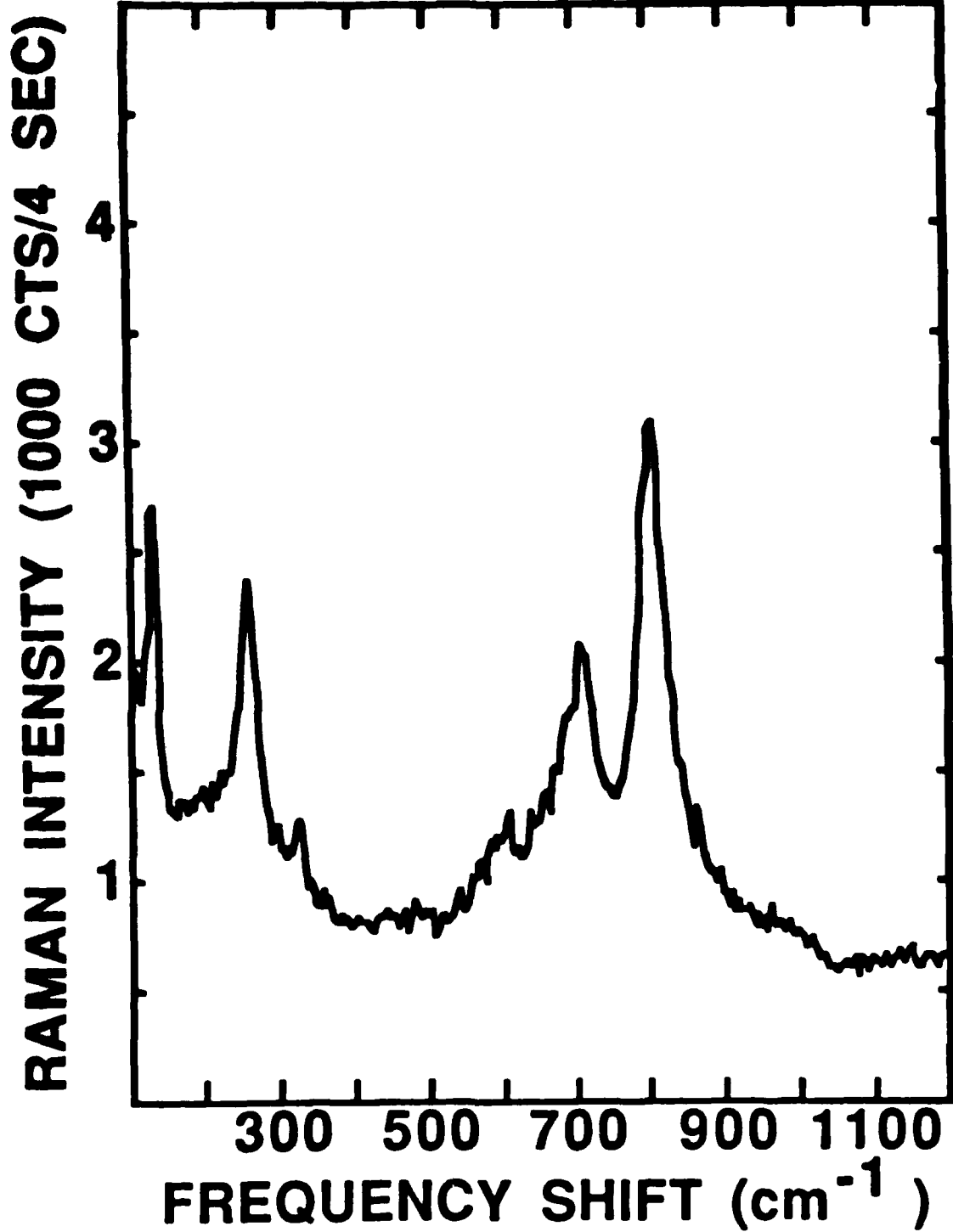


Fig. 5. Raman spectrum of tungsten oxide  $WO_2$ .

# ALUMINUM TUNGSTATE

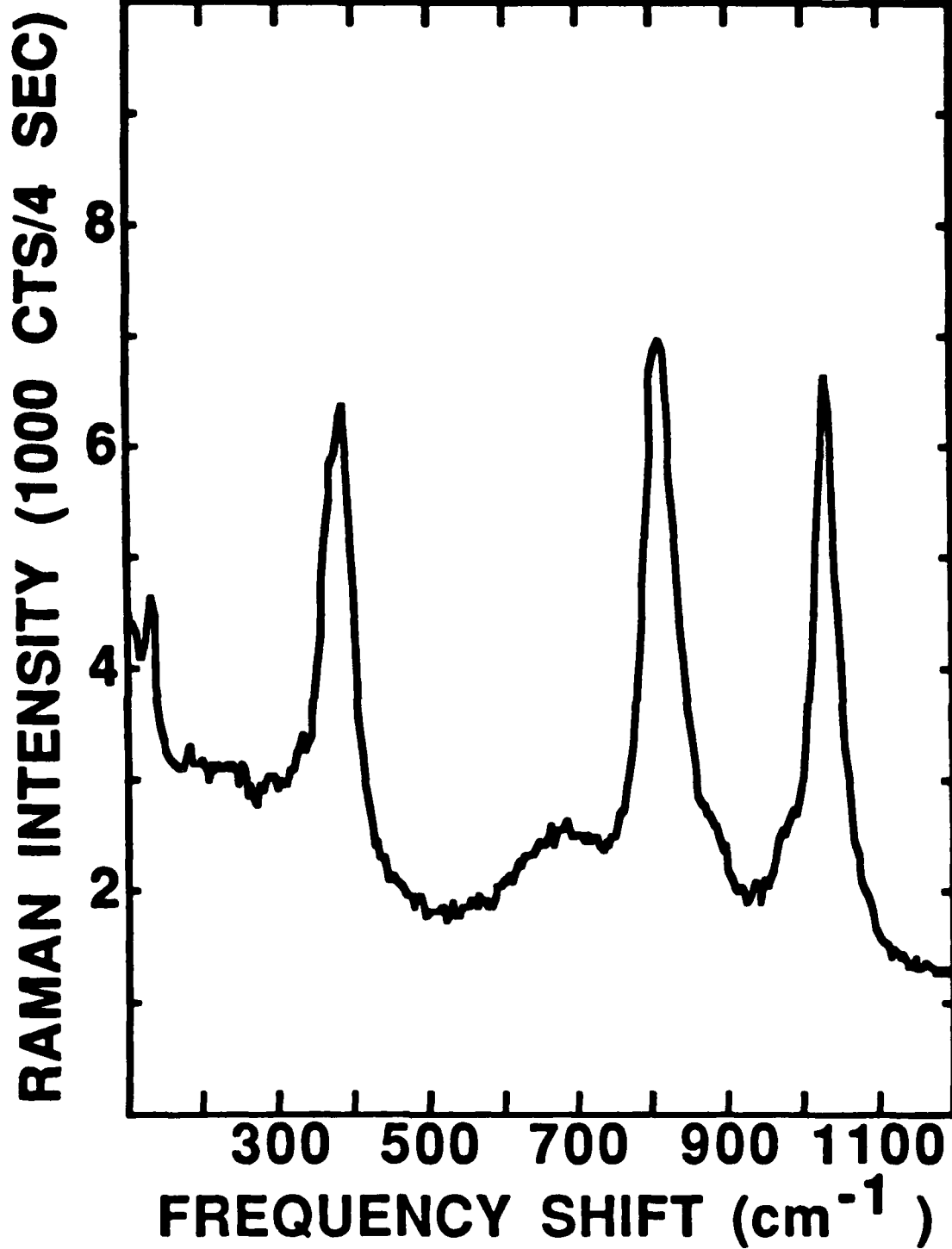


Fig. 6. Raman spectrum of aluminum tungstate.

# ALPHA-ALUMINA

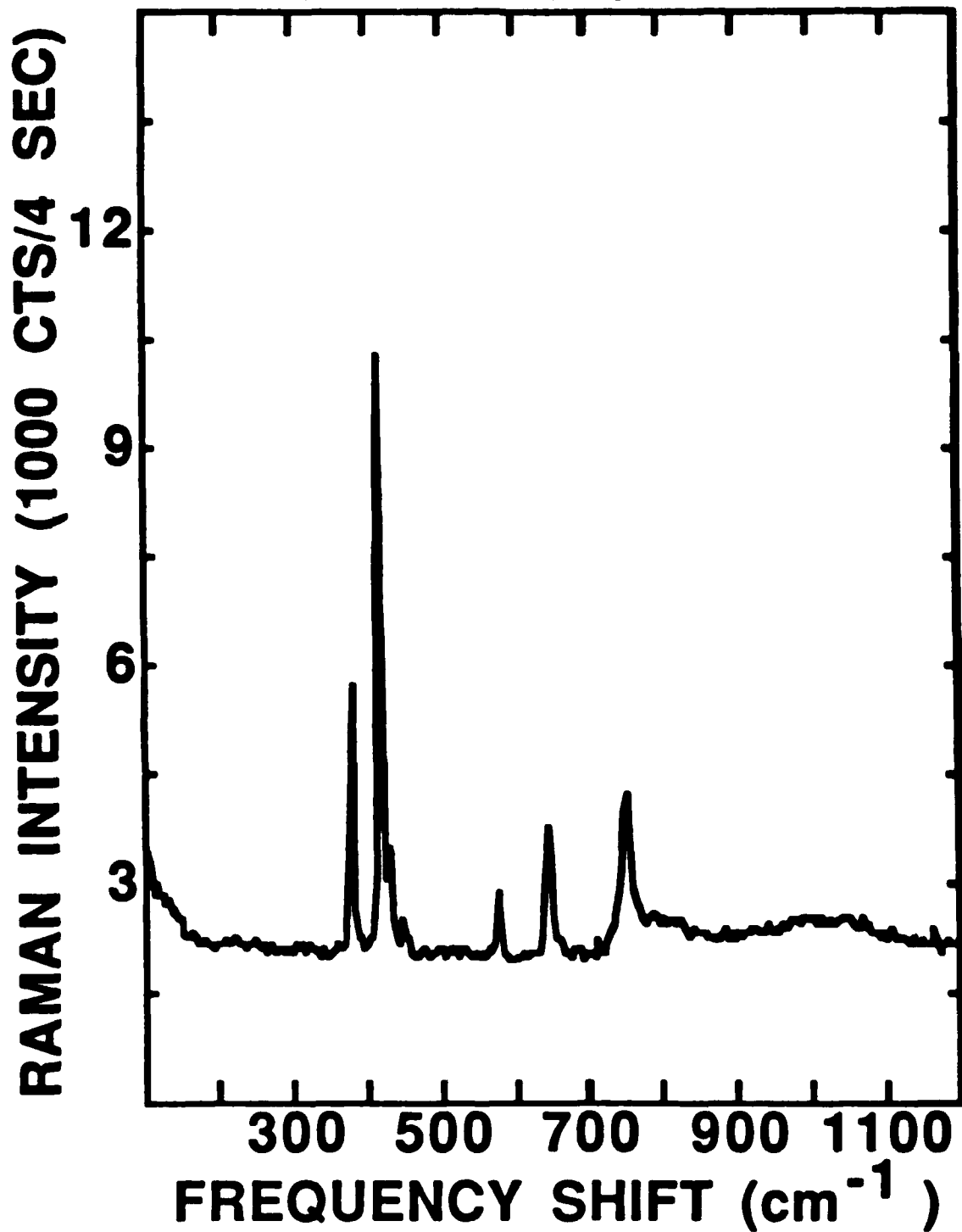


Fig. 7. Raman spectrum of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

# TUNGSTEN (VI) OXIDE

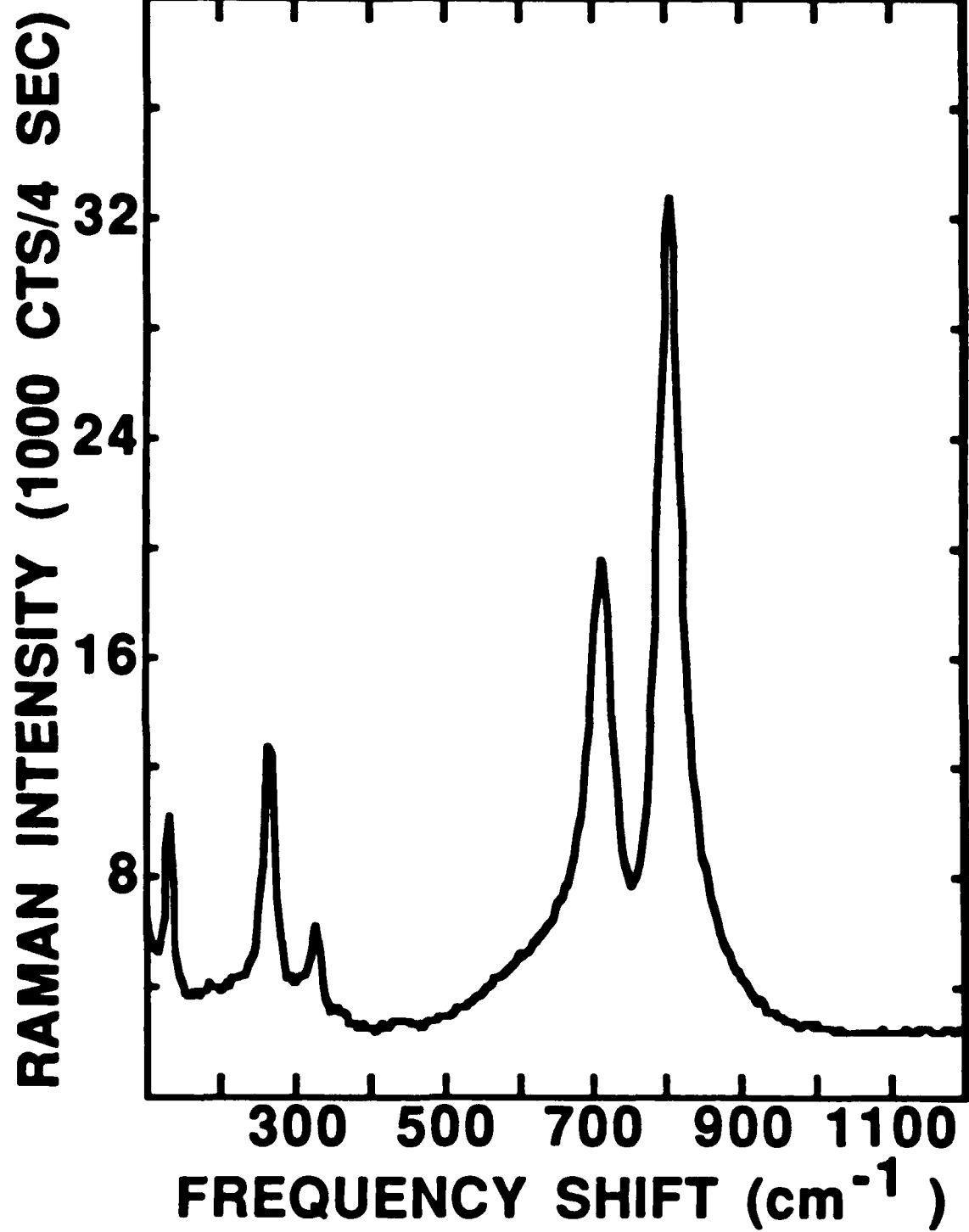


Fig. 8. Raman spectrum of tungsten oxide  $WO_3$ .

# CALCIUM CARBONATE

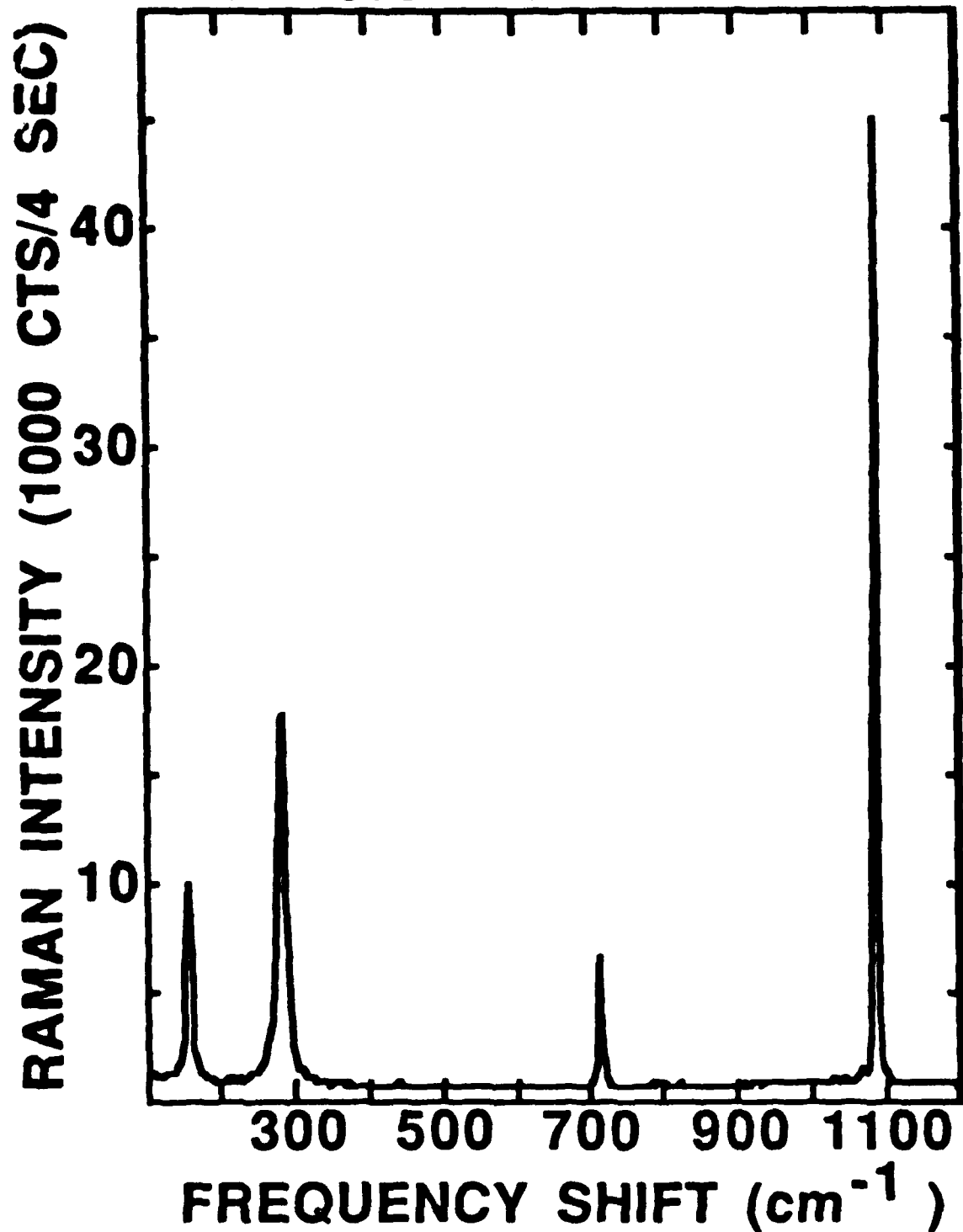


Fig. 9. Raman spectrum of calcium carbonate.

# BARIUM CARBONATE

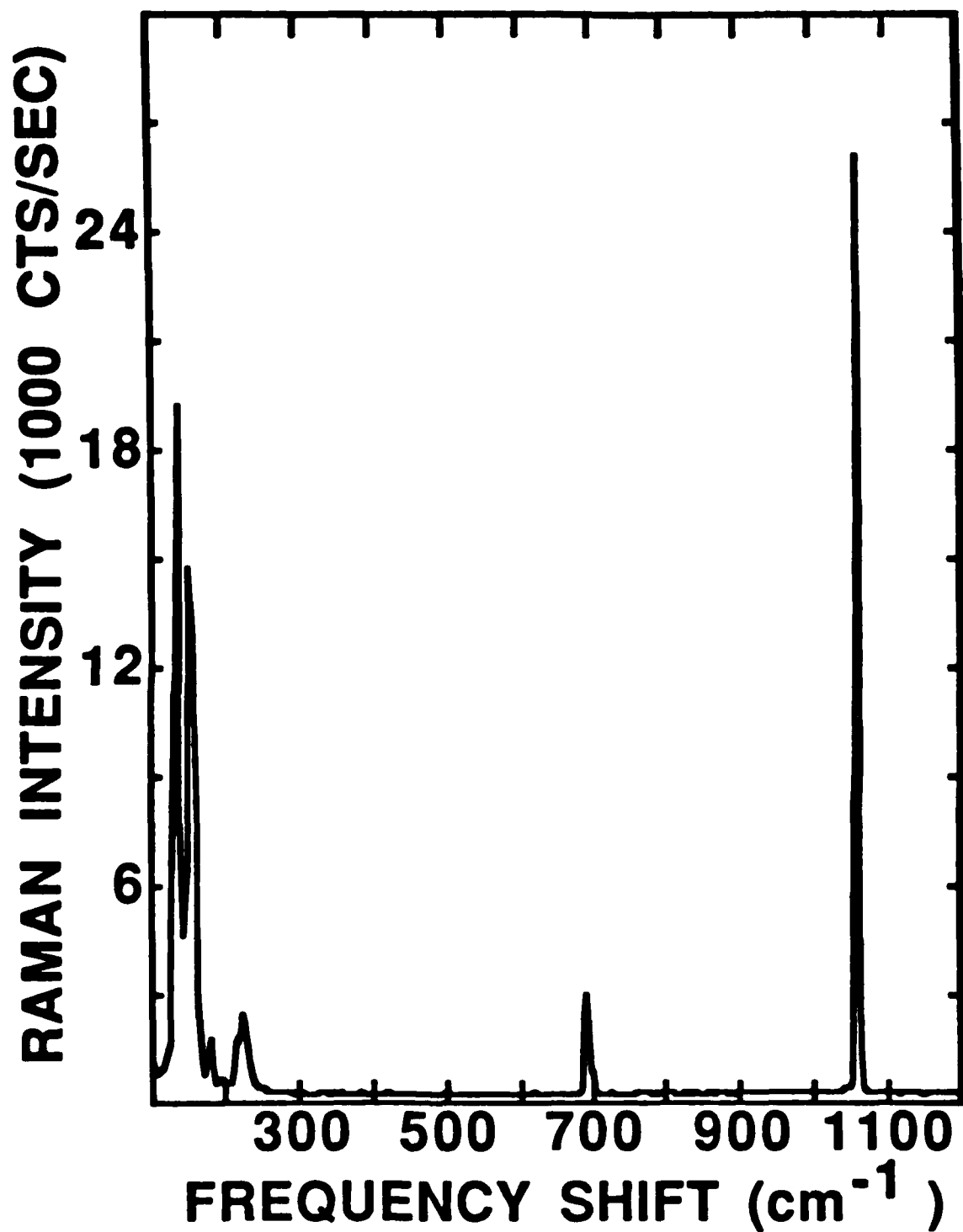


Fig. 10. Raman spectrum of barium carbonate.



# 5-3-2 IMPREGNANT

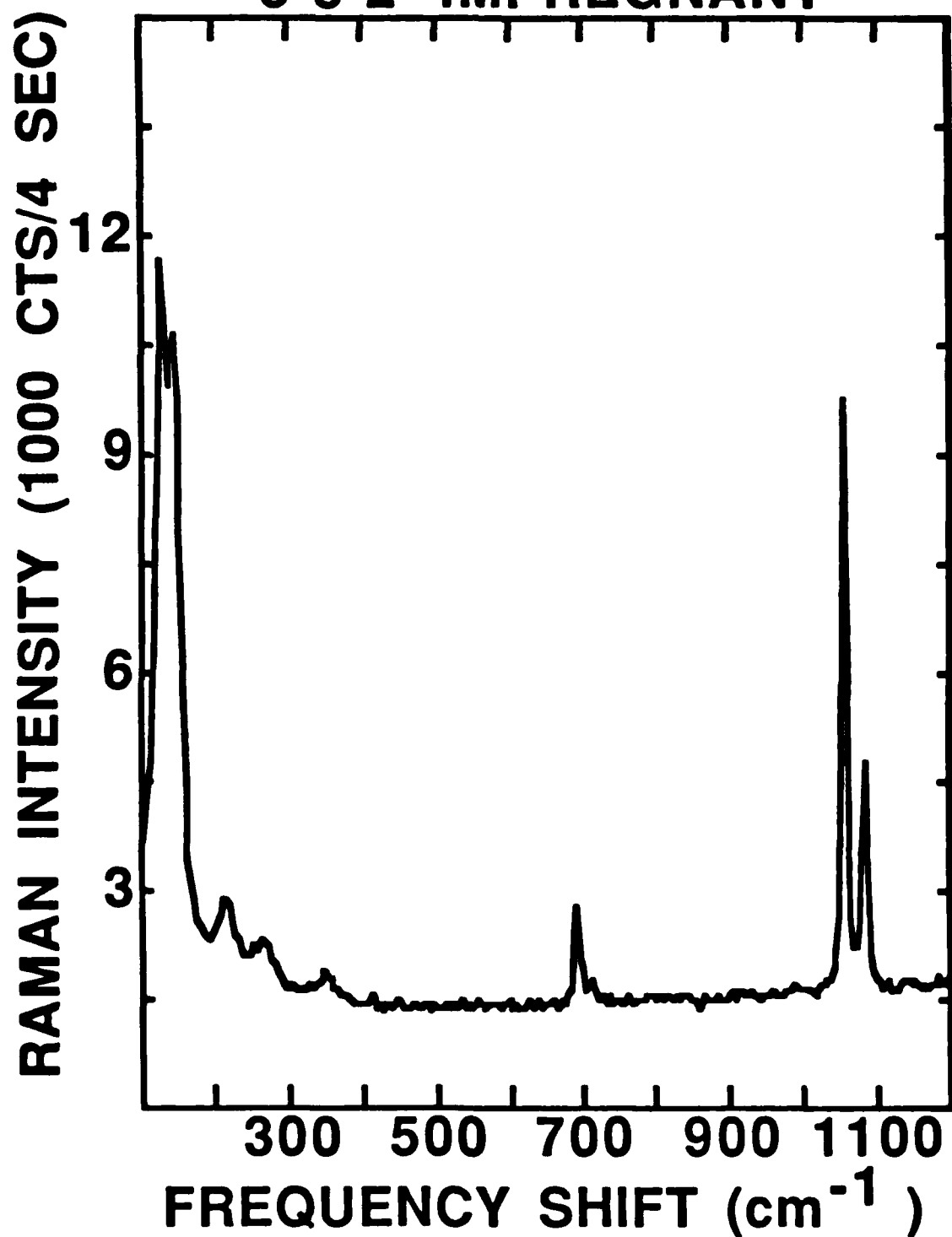


Fig. 11. Raman spectrum of 5-3-2 impregnant powder.

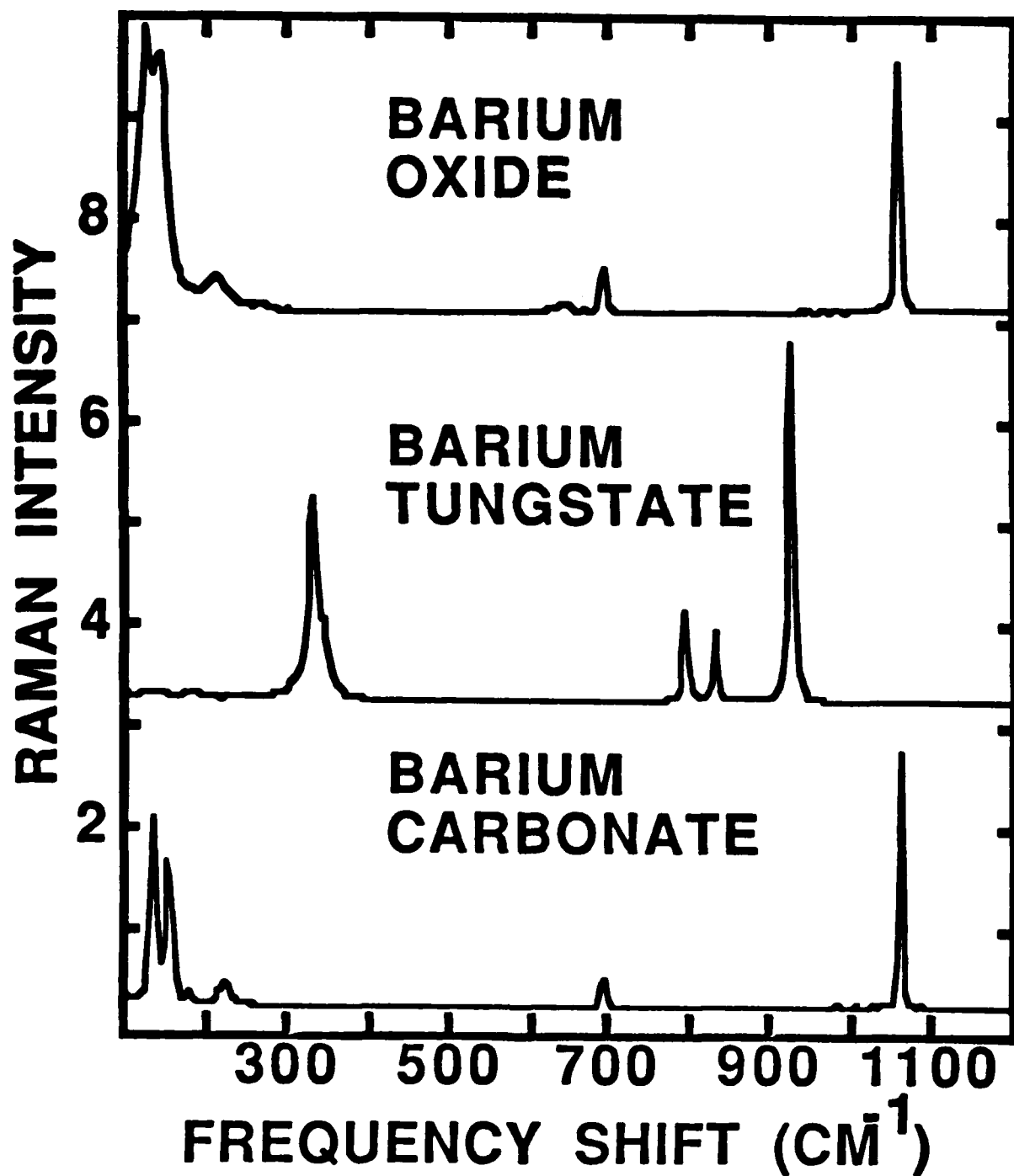


Fig. 12. Raman spectra of various barium compounds having unique spectral signatures.

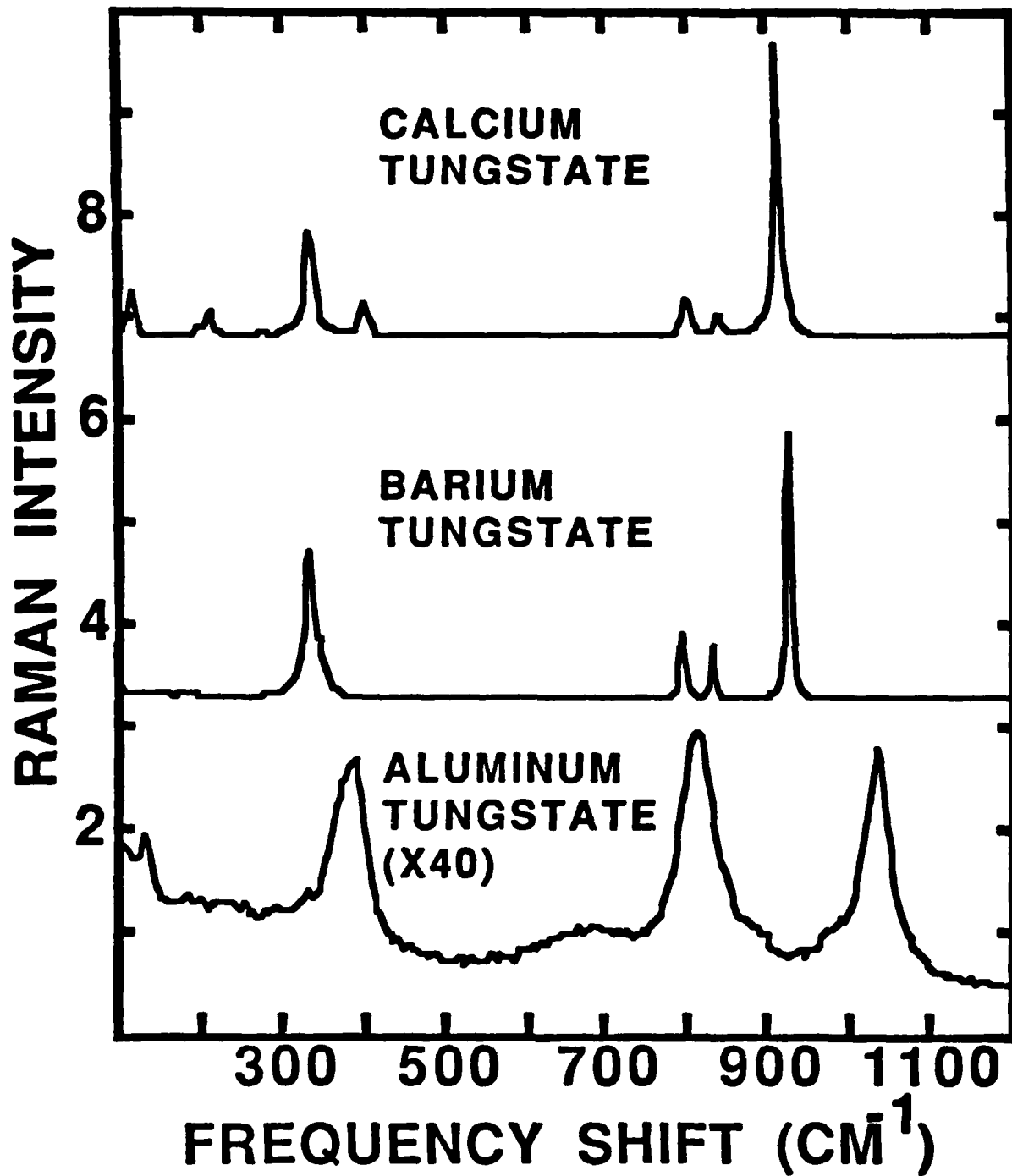


Fig. 13. Raman spectra of various tungstates having unique spectral signatures.

#### IV. CATHODE SPECTRA

Raman data have also been obtained from 5-3-2 impregnant and from several cathode surfaces. In Fig. 14, the spectrum of the 5-3-2 impregnant powder is compared with those of BaO, CaO, and  $\alpha\text{-Al}_2\text{O}_3$ . The data clearly indicate the presence of BaO, but there is little indication for the presence of CaO and no indication of  $\alpha\text{-Al}_2\text{O}_3$ . The absence of pronounced peaks from CaO in the impregnant spectrum is partially explained by its lower nominal concentration in conjunction with the lower scattering strength of the primary peak of CaO compared to that of BaO, as indicated in Table 1. Nevertheless, the data suggest that the 5-3-2 impregnant powder differed from its nominal composition. The absence of peaks for  $\alpha\text{-Al}_2\text{O}_3$  in the impregnant spectrum is probably explained by the  $\text{Al}_2\text{O}_3$  in the impregnant being of a phase other than  $\alpha$ . The spectra of  $\gamma$ - and  $\alpha\text{-Al}_2\text{O}_3$  are compared in Fig. 15. Since only a featureless background signal is observed from  $\gamma\text{-Al}_2\text{O}_3$ , its presence in the impregnant cannot be verified using the Raman technique. It is, however, noteworthy that  $\gamma$ - and  $\alpha\text{-Al}_2\text{O}_3$  have different spectral signatures. Thus, the absence of  $\alpha\text{-Al}_2\text{O}_3$  can be ascertained even though the presence of  $\gamma\text{-Al}_2\text{O}_3$  cannot be determined.

Raman spectra from the surface of a 5-3-2 and a 4-1-1 cathode are compared with the spectrum of 5-3-2 impregnant in Fig. 16. The cathodes studied were new cathodes. While the spectra from the two cathodes have very similar features, they differ radically from that of the impregnant. In an attempt to determine the composition of the cathode surfaces, the 5-3-2 cathode spectrum was compared with the spectra of the

reference materials listed in Table 1. As shown in Fig. 17, a superposition of the spectra from  $WO_2$  (or  $WO_3$ ),  $CaWO_4$ , and  $BaWO_4$  could nearly reproduce the spectral features of the 5-3-2 cathode Raman spectrum. Consequently, we conclude that the Raman analysis indicates the presence of these compounds. More work, however, is required to verify the analysis. A problem encountered in obtaining the Raman data from the cathode surfaces was their high degree of inhomogeneity as revealed by electron micrographs. Because the Raman data were obtained from a surface area having a diameter of approximately 2 micrometers, the sample inhomogeneity was also observed in the scattering data. Figure 18 displays spectra from different portions of the 5-3-2 cathode surface. While these spectra have different features and signal-to-noise ratios, they each have peaks at approximately the same frequency shift positions. The common peaks indicate a relatively uniform chemical composition over the areas investigated, but the spectral differences suggest significant concentration variations on the micrometer scale. The chemical composition suggested by the data is a mixture of tungsten oxide with various amounts of tungstate.

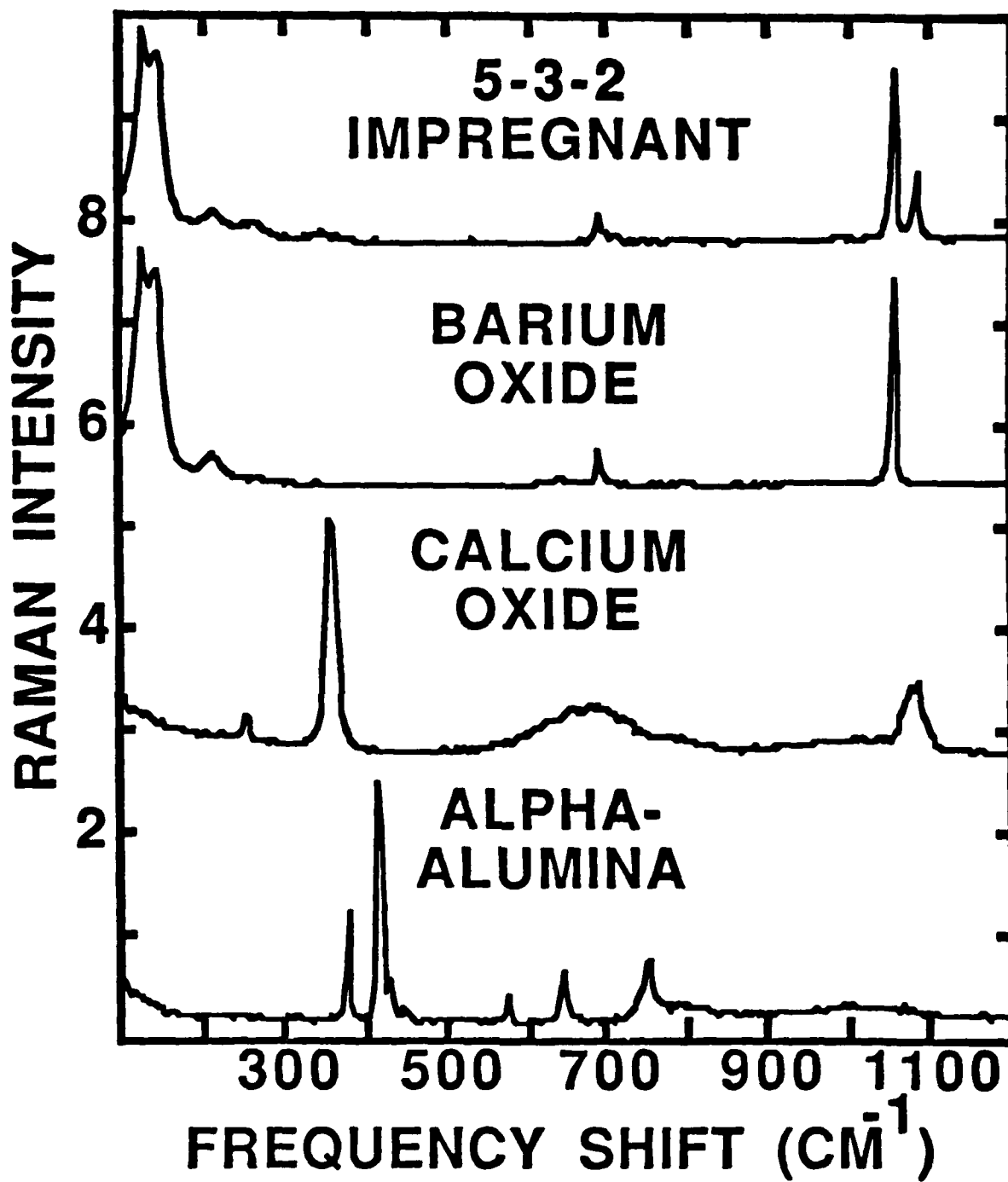


Fig. 14. Raman spectrum of 5-3-2 impregnant compared with spectra of its nominal constituents.

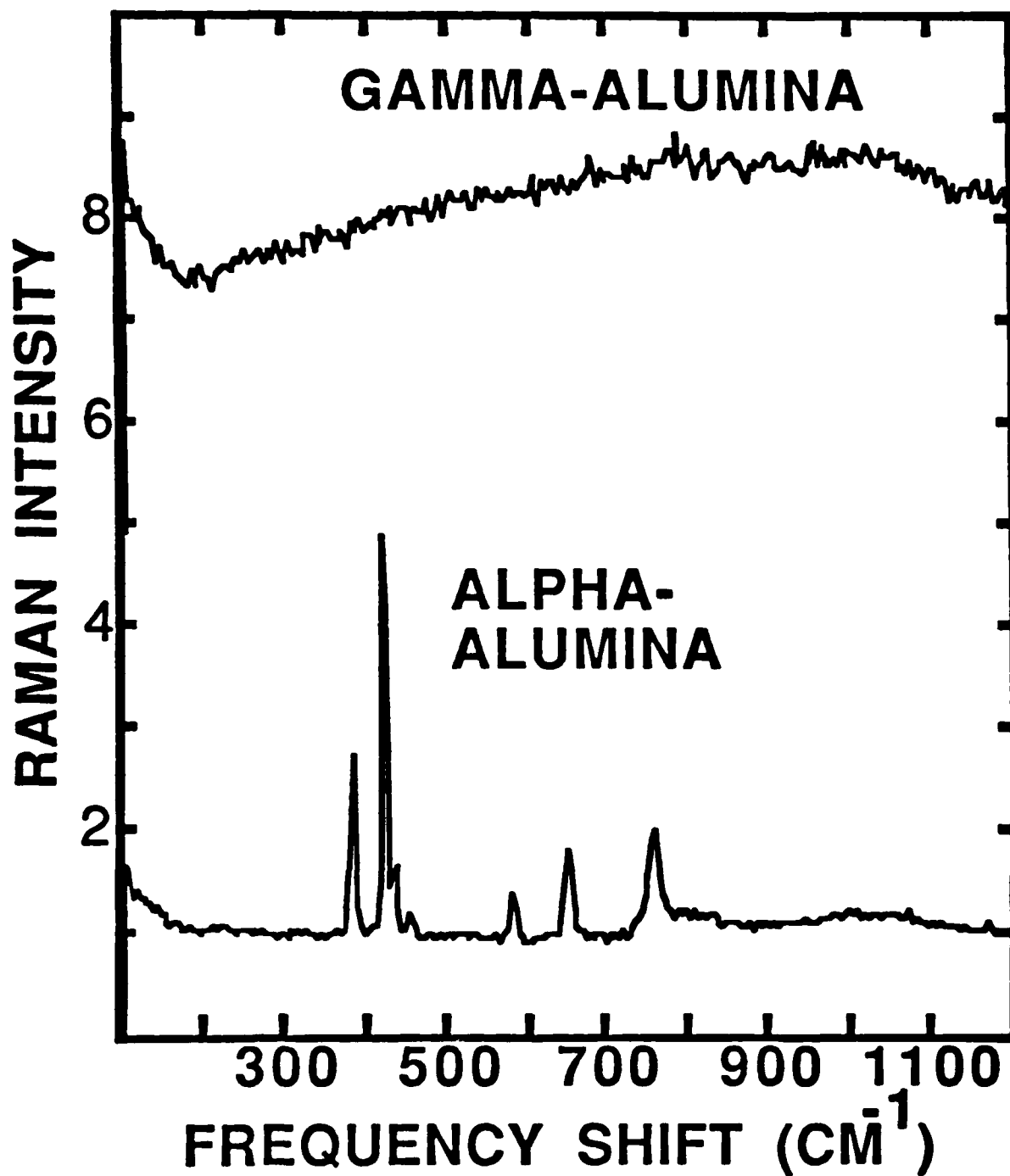


Fig. 15. Raman spectra of  $\gamma$ - and  $\alpha$ - $\text{Al}_2\text{O}_3$ .

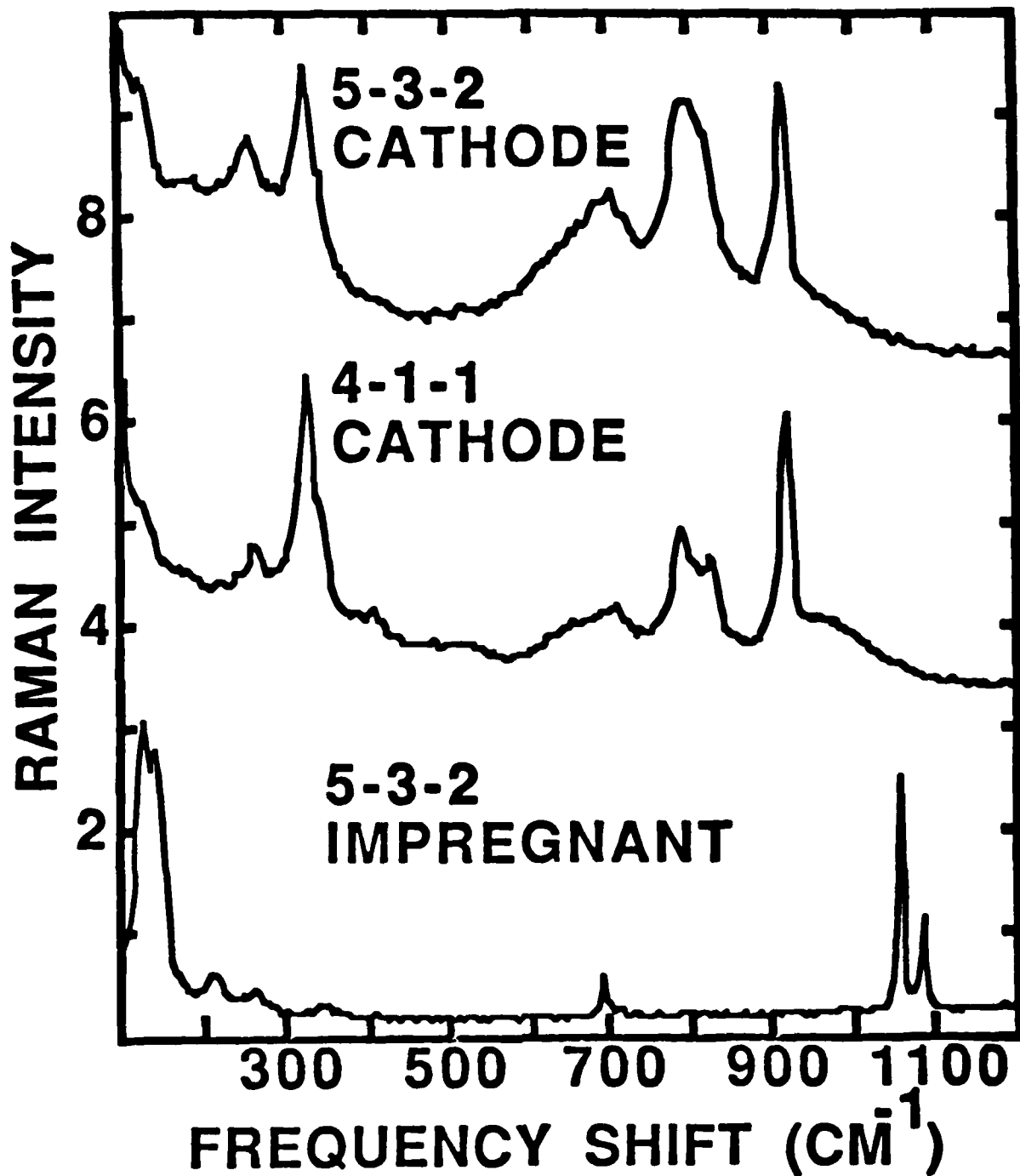


Fig. 16. Raman spectra from the surfaces of 5-3-2 and 4-1-1 cathodes compared to spectrum of 5-3-2 impregnant powder.



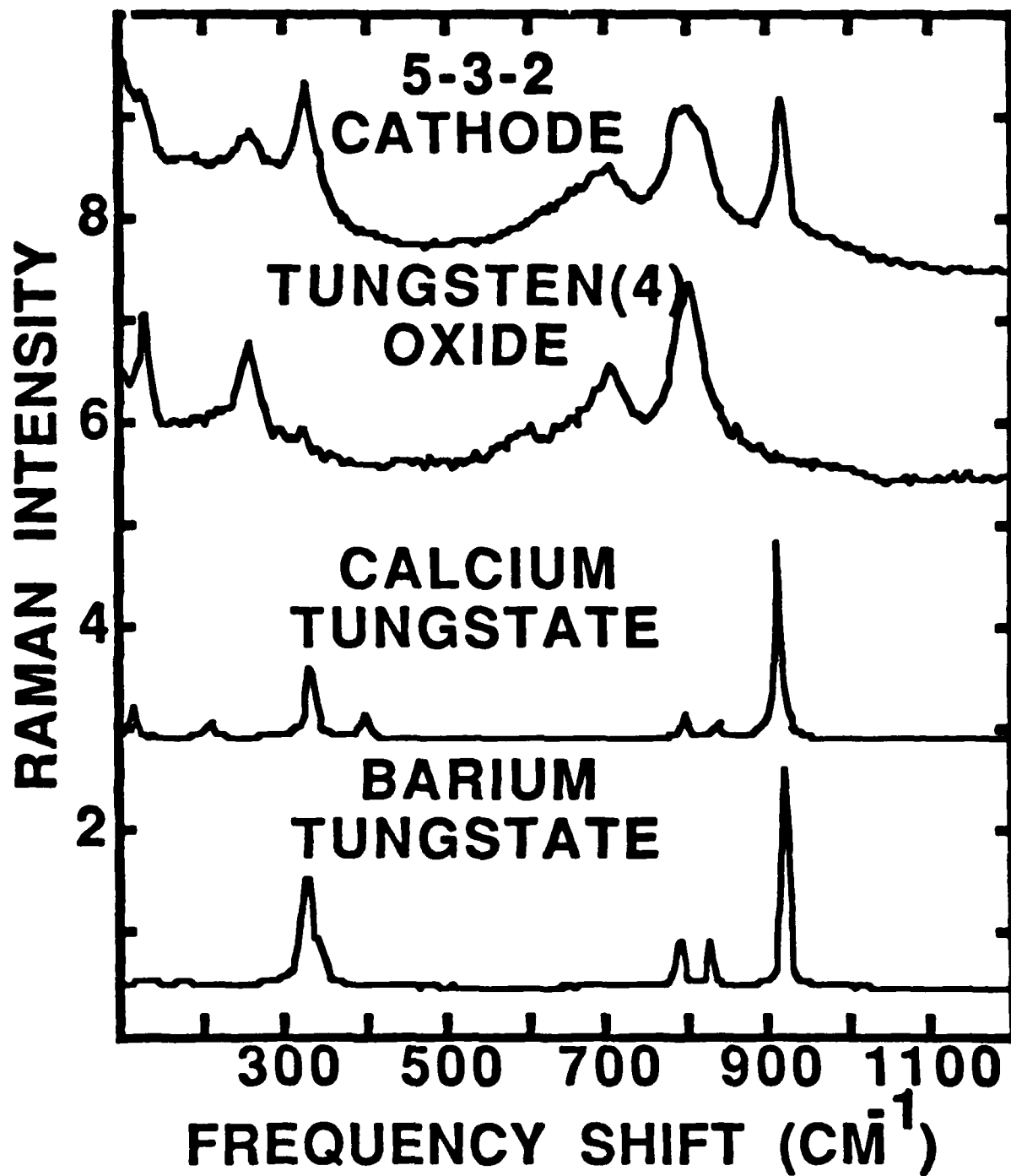


Fig. 17. Raman spectrum from the surface of the 5-3-2 cathode compared with the spectra of selected reference materials.

# SPECTRA FROM DIFFERENT LOCATIONS ON SAME CATHODE

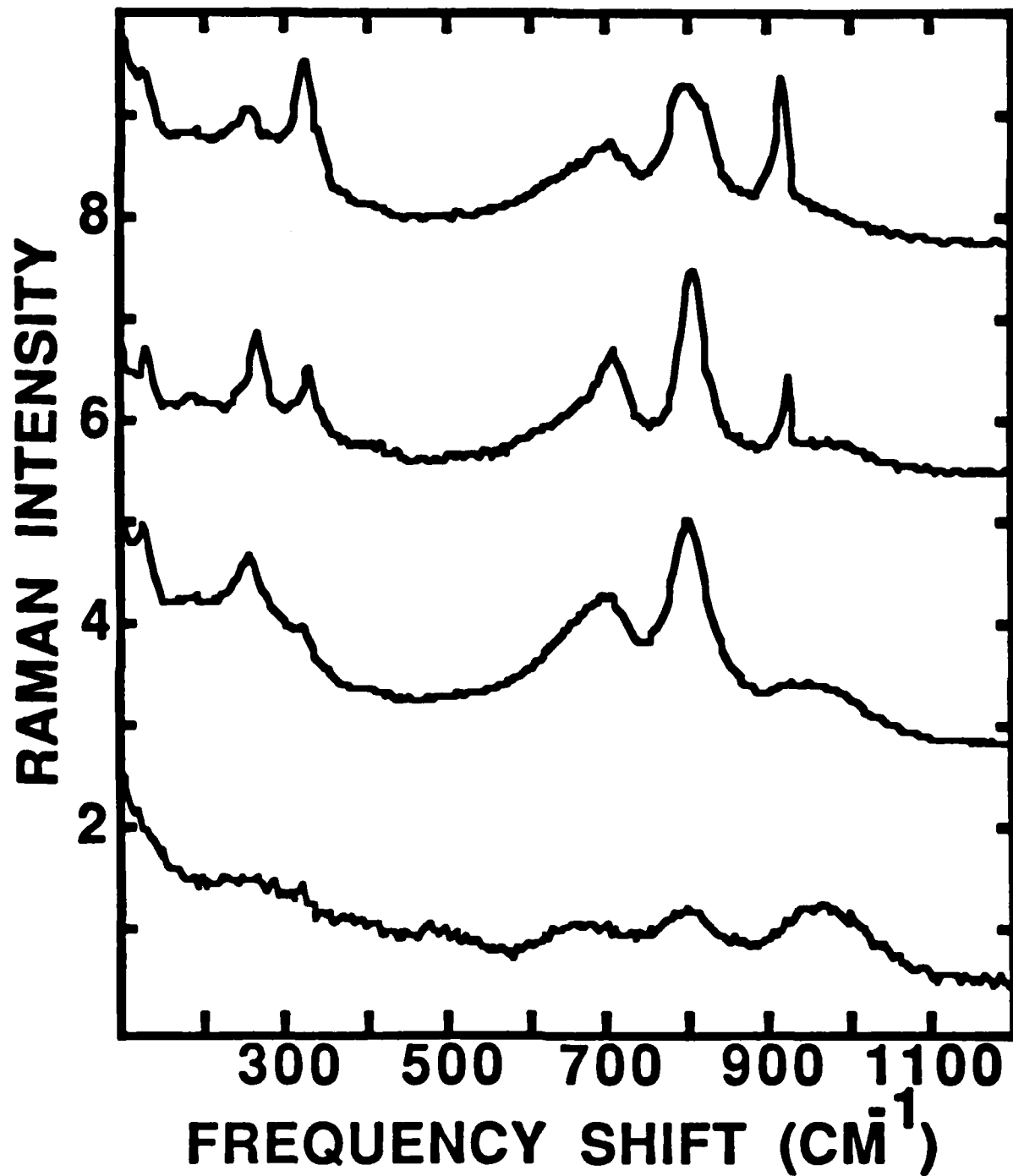


Fig. 18. Raman spectra from different portions of the 5-3-2 cathode surface.

## V. DISCUSSION

The feasibility of obtaining Raman spectra from the surfaces of new dispenser cathodes has been demonstrated. In addition, reference Raman frequency shifts and scattering strengths have been presented for many of the chemical compounds expected to be present at cathode surfaces. While more work is required under carefully controlled environmental conditions before significant conclusions can be drawn regarding cathode chemistry, our preliminary results suggest that future Raman studies of the chemical reactions occurring at cathode surfaces might be highly successful.

A test vehicle could be adapted for optical studies of cathodes during operation. If this were done, several problems would be encountered. First, there would be significant interference with the Raman signals caused by the blackbody radiation emanating from the cathode surface. Calculated blackbody radiation profiles are plotted in Figs. 19 and 20. Figure 19 indicates that the blackbody radiation intensity peaks at wavelengths between 2000-3000 nm (2-3 micrometers) for temperatures between 1000-1500 K. Fortunately, these peaks are significantly red-shifted from the Raman signals initiated by our argon laser operating at a wavelength of 488 nm. Nevertheless, there would still be significant amounts of radiation present in this range of temperature at wavelengths corresponding to the Raman spectra, as indicated in Fig. 20. Since Raman data are frequency shifted from the incident laser frequency, an obvious solution to the problem of blackbody interference is to use an excitation laser with a shorter wavelength. Good

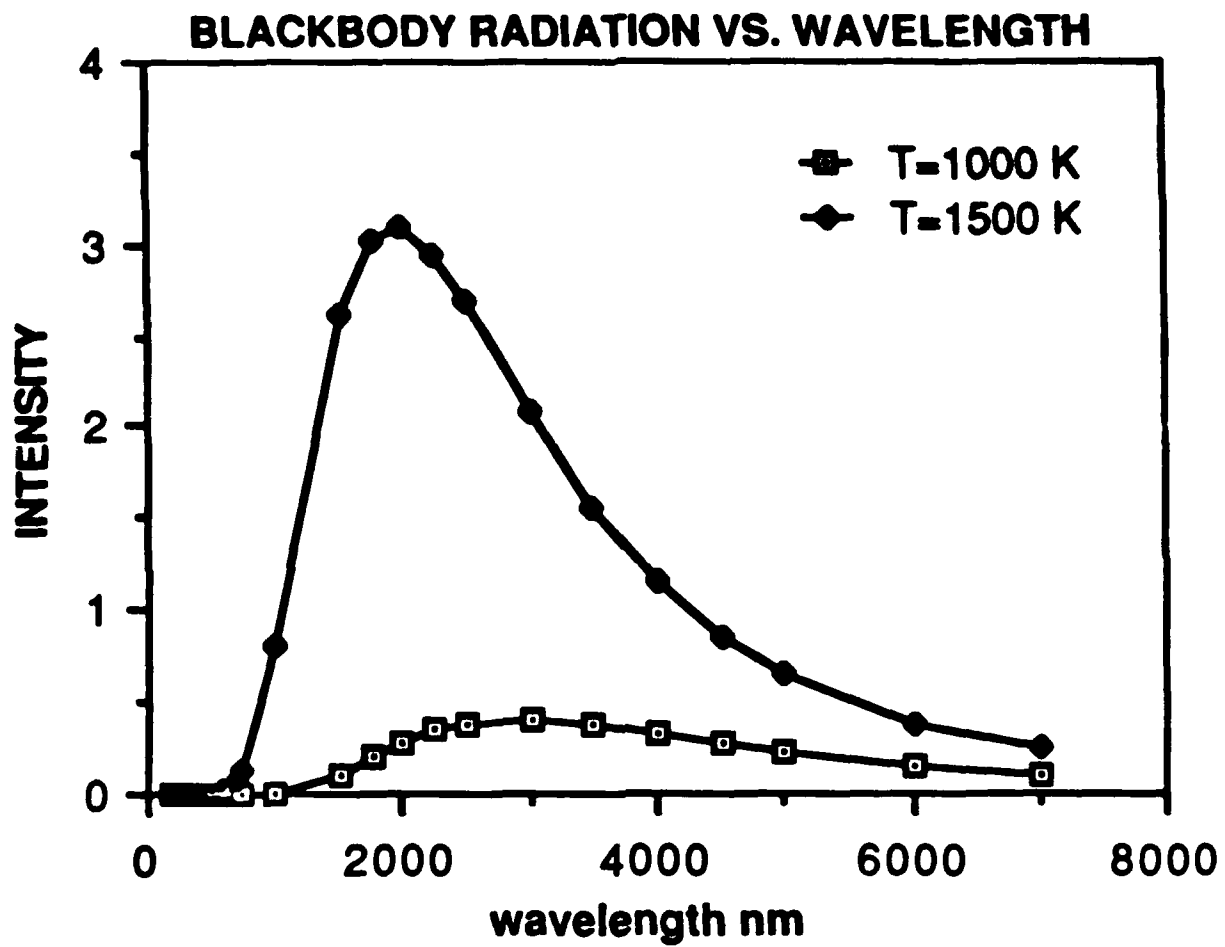


Fig. 19. Calculated blackbody radiation profiles as a function of wavelengths for temperatures of 1000 K and 1500 K.

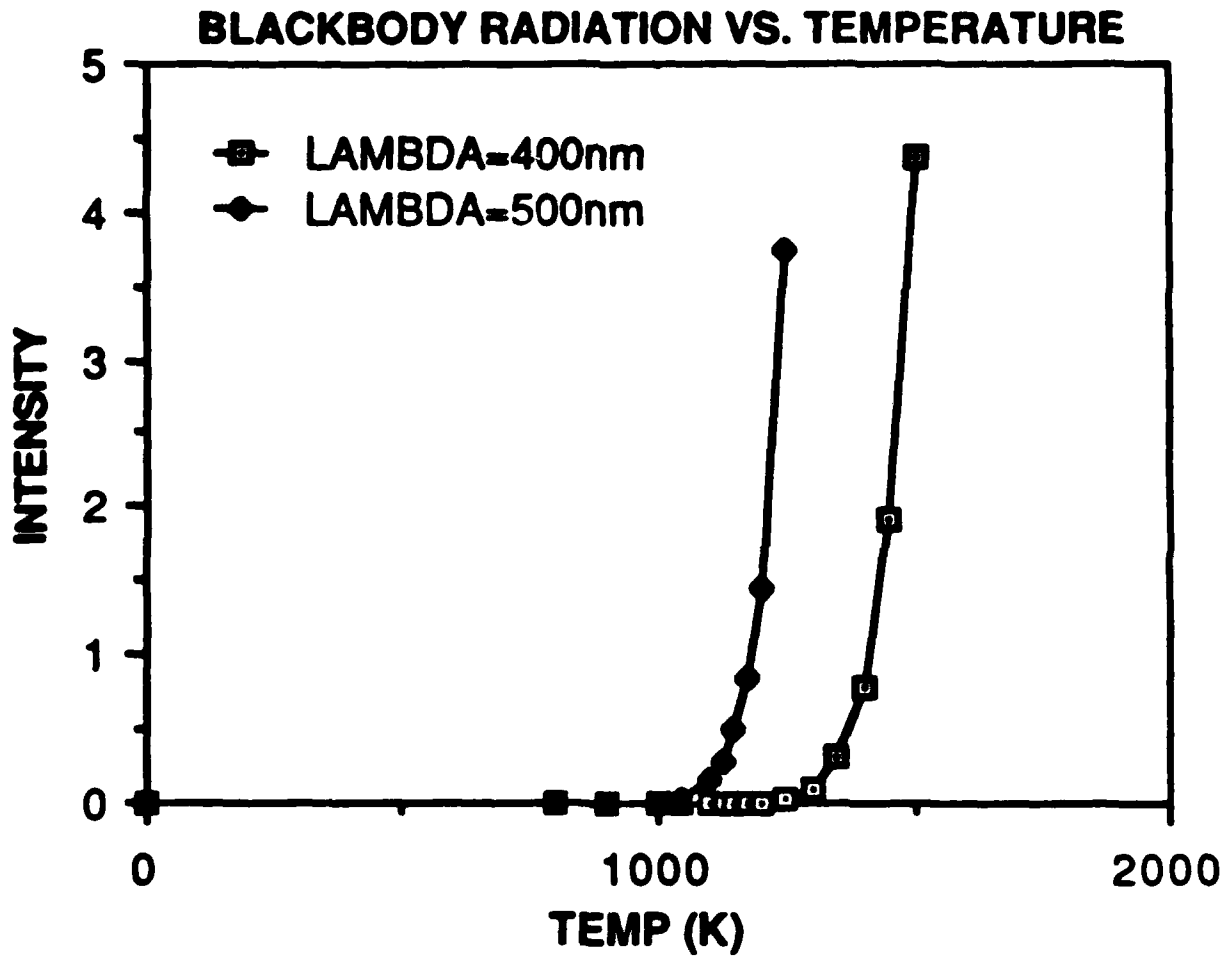


Fig. 20. Calculated blackbody radiation profiles as a function of temperature for wavelengths of 400 nm and 500 nm.

candidates would be either an excimer or a frequency-tripled Nd:YAG laser. An alternative approach to minimizing blackbody radiation interference is to utilize a pulsed laser with high peak power and a low duty cycle in conjunction with gated electronic detection to time discriminate against the continuous blackbody radiation in favor of the Raman signal. A combination of the two approaches can be expected to yield Raman spectra at temperatures approaching 1500 K.

A second problem which can be expected if a test vehicle is adapted for in-situ Raman studies is a need for increased sensitivity. If Ba-O monolayers at the cathode surface are to be probed effectively, a Raman apparatus with a sensitivity of 10-100 times that of the system used in this study would probably be required. Instrumental modifications could provide this amount of sensitivity improvement. We anticipate adapting a modified Raman apparatus employing multichannel detection and a pulsed laser system for future experiments. A properly designed multichannel detector can be expected to provide a signal-to-noise ratio improvement given by the square root of the number of channels in the detector array. Detection of Raman spectra from monolayer amounts of material using multichannel arrays has already been reported. The Raman signal obtained with a high peak power pulsed laser should increase by an amount corresponding to the ratio of the peak power compared to the CW power level of 400 mW used in our experiments if gated detection is also used. These instrumental modifications should significantly improve the chemical sensitivity, time response, and high temperature capability of our present Raman system to a level which should make meaningful in-situ Raman studies of cathodes feasible.

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