THE RAMAN SPECTRUM OF BERYLLIUM SILICATE

By P. S. NARAYANAN

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

1. INTRODUCTION

THE existence of a large variety of silicates is mainly a result of the wide range of silicon-oxygen arrangement which is possible. In spite of the apparent complexity, the principles governing their structure are very simple. The structure of these minerals may in all cases be regarded as based on the formation of co-ordinate lattices of large anions about small cations. The O^{--} ions being of much greater size than any of the positive ions occurring in the silicates, they form the skeleton of the whole structure, the $O - O$ distance being always about $2 \cdot 6$–$2 \cdot 8$ Å.U.

In spite of our detailed knowledge of the structure of the silicates and the fact that many of the silicates could be had in transparent form, very little work appears to have been done on their Raman spectra. Nisi was the only one to investigate the Raman effect in a large number of silicates, namely phenacite, zircon, beryl, danburite, tourmaline, topaz and olivine. In every case he reported only half a dozen frequency shifts; this is presumably due to the feebleness of scattering in those crystals and to the use of the visible radiations of the mercury arc for obtaining the Raman spectra. If one takes into consideration the complexity of the silicates and to the large number of atoms in the unit cell, it is obvious that the data obtained by Nisi are incomplete. That it is so, is shown by the recent investigations of R. S. Krishnan (1947) on topaz using $\lambda 2537$ as exciter. No less than 32 Raman shifts were recorded compared to the 11 previously reported. A satisfactory interpretation of the vibration spectrum of any silicate in terms of its structure is possible only if we have complete data for a series of silicates. It was therefore felt desirable to reinvestigate the Raman effect in a number of silicates using the ultraviolet technique. A preliminary report of the results obtained with one of the simplest of the silicates, namely phenacite, is made here.

2. EXPERIMENTAL RESULTS

The Raman spectrum of phenacite or beryllium silicate (Be_2SiO_4) was recorded using the resonance radiation of the mercury arc and the Rasetti

technique as developed in this laboratory. The author is indebte
Prof. C. V. Raman for placing at his disposal a colourless, clear and well
formed crystal of phenacite which made this study possible. The direction
of illumination and observation were entirely arbitrary, and no great impor-
tance could therefore be attached to the relative intensities recorded. A
correlation of the observed lines with the possible modes of vibration would
scarcely be possible till the polarization studies are completed. The Raman
spectrum is reproduced in Fig. 1 in Plate. The frequency shifts of the
observed Raman lines and the infra-red reflection maxima (Schaefer,
Matossi and Wirtz) are listed in Table I.

TABLE I

Raman spectrum of phenacite

Frequency shifts cm.$^{-1}$	Infra-red maxima (cm.$^{-1}$)	Frequency shifts cm.$^{-1}$	Infra-red maxima (cm.$^{-1}$)
161 (2)	..	667·5 (1)	599
184 (1)	..	685·5 (1)	
222·6 (5)		705 (2)	692
230·0 (2)	..		
254·7 (1)	..	726 (1)	723
279 (2)	..	776 (3)	743
348 (2)	..	805 (1)	788
383 (4)	..	879 (10)	914
		918 (7)	
445·5 (4)	..	937 (5)	957
465 (1)	..	949·2 (5)	
485 (1)	..	1010 (1)	990
			1014
526 (3)	..	1022 (1)	1040
580 (1)	575		1093

Of the 25 Raman lines observed by the author, only the intense one
numbering about 8 were recorded by Nisi. Nisi reported a frequency shift
of 3600 cm.$^{-1}$ in the spectrum of phenacite. The author was unable to confirm
the existence of this line and it is also improbable that such a line exists in
phenacite as there is no (OH) group in it.

The most striking feature about the spectrum of Be_2SiO_4 is the extreme
sharpness of all the 24 lines recorded contrary to what is observed in glasses
and in quartz (see the microphotometer record reproduced in Fig. 2).
However, the lines are intrinsically feeble in intensity, as exposures of the
order of 2 days were found to be necessary even with the ultraviolet excitation.
The transmission in the ultraviolet was good enough to justify our neglecting
any influence it might have had on the feebleness of the scattered light.
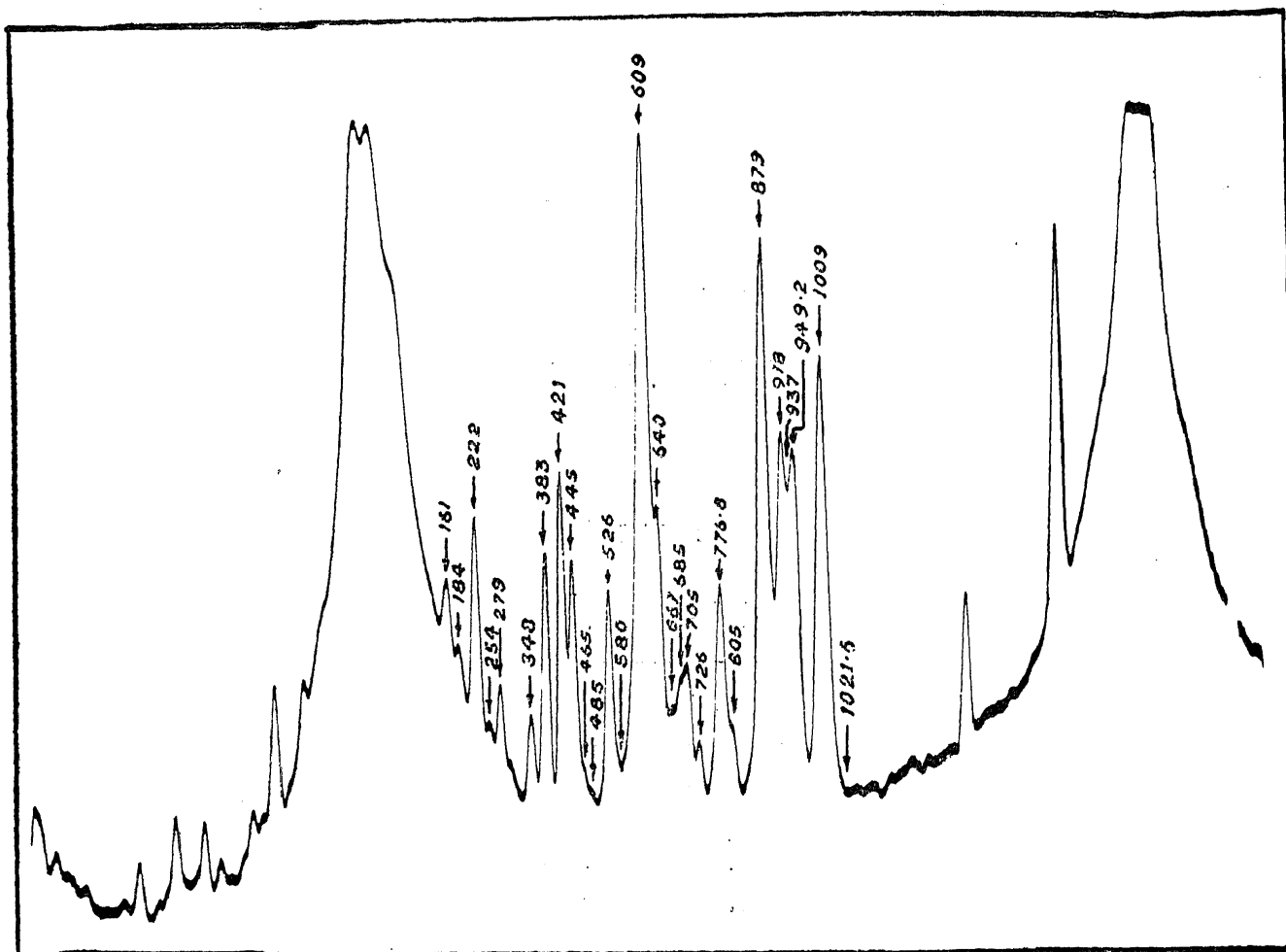
FIG. 2. Microphotometer curve of the Raman spectrum of beryllium silicate

3. DISCUSSION

Phenacite or Be_2SiO_4 is an orthosilicate belonging to the hexagonal alternating class of the rhombohedral system. The crystal structure has been studied by W. L. Bragg (1927), Bragg and Zachariasen (1930) and Gottfried (1927). It is isomorphous with dioptase, willemite and troostite and its space group is C_{3i}, the symmetry elements being E, $2S_6$, $2C_3$ and i. The vibrations of the 6 molecules in the unit cell (external and internal) fall under four classes, 2 being symmetrical and the other two doubly degenerate. It is easy to see that because of the low symmetry, the possible number of vibrations is large, and the presence of the centre of symmetry makes the infra-red maxima and Raman shifts complementary, as theoretically the two classes of vibration A_g and E_g are allowed only in Raman effect and A_u and E_u only in the infra-red. For a proper assignment of the Raman frequencies and also for an explanation of the approximate coincidences noticed between the infra-red maxima and the Raman lines, polarization data are necessary.
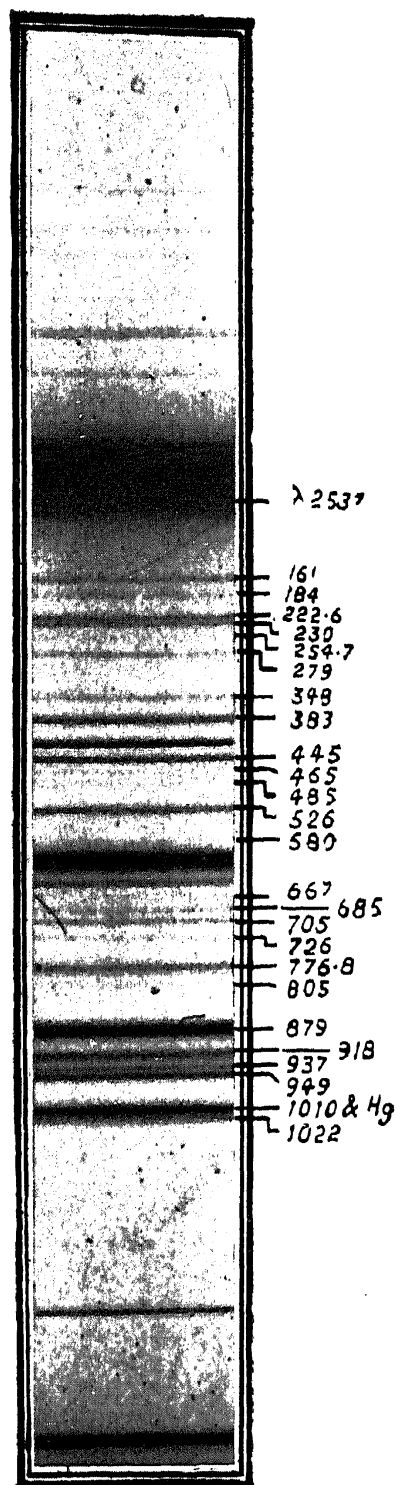
FIG. 1.   Raman spectrum of beryllium silicate taken with the medium
spectrograph

It is interesting to compare the Raman spectra of the various silicates and that of quartz. The results so far obtained are collected together in a diagrammatic form in Figs. 3 & 4 to show the general similarity of the Raman spectra of the different silicates. In all cases the frequency shifts are limited to the region 100-1100 cm.$^{-1}$ Fig. 3 represents the spectra of crystals
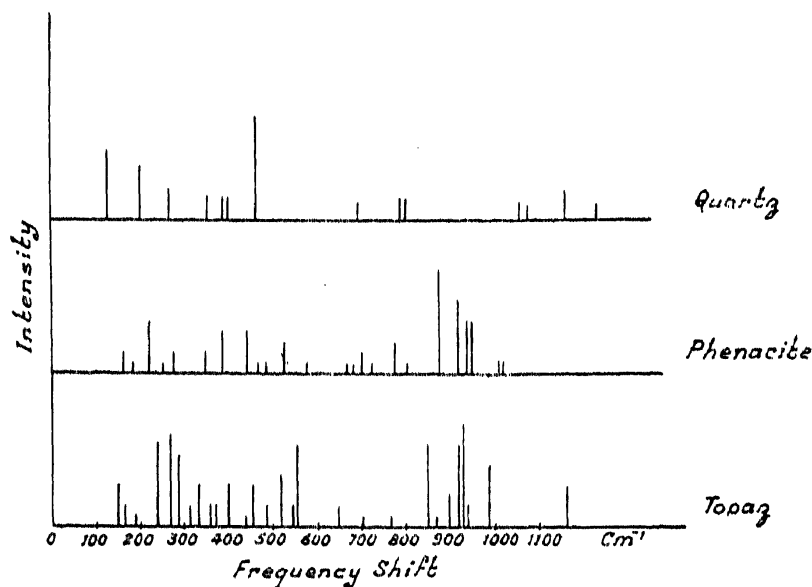

FIG. 3. Chart showing the Raman spectra of Quartz, Phenacite and Topaz

which have been studied using $\lambda\,2537$, and shows the grouping and intensity distribution of lines in a similar manner. The data shown in Fig. 4 were taken from the paper by Nisi (1932) and their incompleteness is quite evident.

In conclusion, the author wishes to express his thanks to Prof. R. S. Krishnan for some useful discussions.
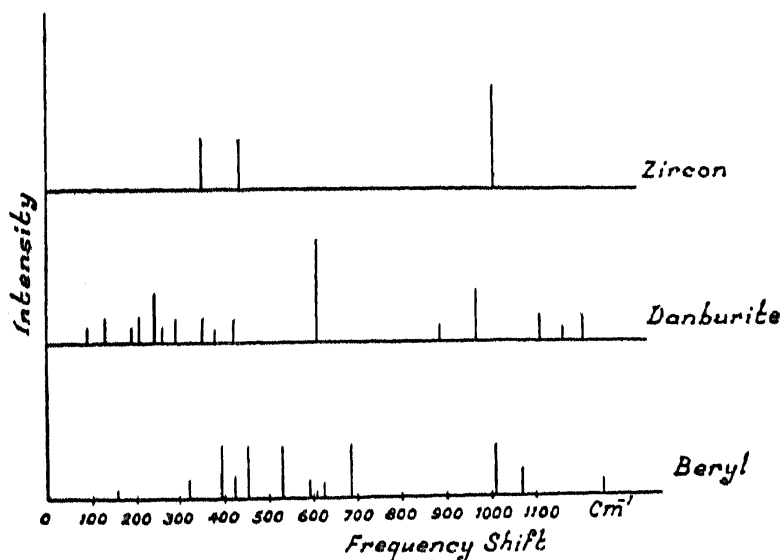

FIG. 4. Diagrammatic representation of the Raman spectra of zircon, danburite and beryl

SUMMARY

The Raman spectrum of beryllium silicate has been studied using the resonance radiation of mercury as exciter. The spectrum exhibits 25 Raman lines, 17 of which have been recorded for the first time. The Raman lines are extremely sharp. The observed spectrum has been compared with the spectra of other silicates.

REFERENCES

W. L. Bragg	..	*The Structure of Minerals.*
Nisi	..	*Proc. Phys. Math. Soc. Japan,* Series 3, 1932, **14**, 214.
Schaefer, Matossi and Wirtz	..	*Zeits. f. Physik,* 1934, **89**, 210.
W. L. Bragg	..	*Proc. Roy. Soc.,* Lond. A, 1927, **113**, 642.
—— and Zachariasen	..	*Zeits. f. Physik,* 1930, **72**, 518.
C. Gottfried	..	*N. Jb. Min. Beil. Bd.,* 1927, **55 A**, 393.
F. Matossi	..	*J. Chem. Phys.,* 1949, **17**, 679.
R. S. Krishnan	..	*Proc. Ind. Acad. Sci.,* 1947, **25**, 460.

ERRATUM

Vol. XXXI, No. 1, January 1950

Page 31, line 5, *delete* ' (6-hydroxy galangin) '.