

*The mineralogy of the potassium–barium feldspar series**I. The determination of the optical properties of natural members*

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*Summary.* Variation diagrams for the optic properties and densities of natural specimens within the series have been determined. They focus attention on two composition regions at about 45 % Cn and 65 % Cn. The significance of the first of these is uncertain, but it is suggested that the discontinuity at 65 % Cn is related to structural changes that take place at this composition.

**B**ARIUM-ORTHOCLASES, hyalophanes, and celsians are thought to form a series in the feldspar group ranging from potash feldspar ( $\text{KAlSi}_3\text{O}_8$ ) to barium feldspar ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ). The replacement of potassium by barium is accompanied by the substitution of aluminium for silicon, suggesting an analogy with the commoner plagioclase series. An important distinction, however, lies in the large size of the barium ion, which imposes monoclinic symmetry on the feldspar framework, in contrast to the triclinic symmetry of the plagioclases. Despite its mineralogical interest and its relationship to the alkali and plagioclase series, there has been no systematic study of the potassium–barium feldspar series, probably because of the relative rarity of its members. Individual members of the series have, from time to time, been described, and there have been sporadic attempts to correlate their properties. The present work is based on a collection of natural specimens over the whole composition field. Whilst this collection is not so comprehensive as could be desired, and there are some gaps in continuity across the field, sufficient specimens are available to make a general survey. At the same time, work has been carried out on synthetic materials to obtain supplementary information.

In this paper the results of the determination of the optical properties of the natural specimens are presented, together with density measurements. With the small amount of materials available, and the possibility of zoning in some specimens, it was essential that as many

observations as possible should be made upon the same crystal of the feldspar. To this end, a spindle stage for use upon the polarizing microscope has been designed by the author and this is described in another paper (Roy, in press).

The natural specimens used in the present work are similar to those mentioned by Gay (1965), and the same reference numbers will be used. The compositions quoted are in mol. % celsian unless otherwise stated.

### *Experimental results*

The optical variation diagrams proposed by previous workers appear to have been constructed from very little data. Probably the most complete study is by Yosimura (1939) who shows variation diagrams for birefringence,  $2V$ , extinction angles, and the principal refractive indices. These show smooth variations over the series except in the region about 40–45 % Cn where there is a discontinuity. Other workers have found it difficult to reconcile measurements for their particular specimens with Yosimura's diagrams (e.g. Segnit, 1946), though later work by Vermaas (1953) using determinative curves constructed from X-ray powder data appears to support the existence of a discontinuity at about the composition suggested by Yosimura (1939). More recent diffractometer work (Gay, 1965) has thrown doubt on the validity of the determinative curves proposed by Vermaas. Thus the question of a discontinuity in the series and of a miscibility gap remains open, and further evidence will be provided by the present studies.

In this paper all optical constants, unless otherwise stated, have been determined using the spindle-stage; the BaO content has been obtained by electron probe analysis on the grain used for optical determinations. Baryte and orthoclase were used as the respective standards. The ideal compositions for orthoclase and celsian were assumed in calculating the atomic-number and absorption-correction factors. The celsian-contents for the members of the series are computed on the same assumption although feldspars do not usually conform to this ideal; during the present investigation there was no other alternative because the amount of material available was not sufficient for conventional chemical analysis.

The values of the *principal refractive indices* are given in table I, and are plotted with some values from the literature in fig. 1. The variations differ from those of Yosimura in that they are not linear, and they show no obvious discontinuity at 40–45 % Cn. The curves have been drawn to show a change in trend at this point, which would appear to be significant if only the present observations are considered. If the values

from the more recent literature are taken into account, with the greater spread of observations, it would appear to be possible to draw a smooth continuous variation over the whole series.

TABLE I. Optic constants and densities of the natural specimens of the hyalophane-celsian series.

Sample nos.	Composition (mol. %)		Indices of refraction†			$2V_{\alpha} \ddagger$ (obs.)	$\alpha: [100]$	$\gamma: [100]$	Density (gm/cm <sup>3</sup> )	
	Cn	Or	$\alpha$	$\beta$	$\gamma$					$(\gamma - \alpha)$
Orthoclase ...	—	88.1	1.520	1.523	1.524	0.004	40.0	+5.0	—	2.563
Orthoclase ...	—	93.7	—	—	—	—	—	+3.6	—	—
(10)80199 ...	2.2	—	1.518	1.521	1.524	0.006	62.6	+2.0	—	2.576
g11156 ...	11.5	84.8	1.526	1.529	1.532	0.006	66.9	0.0	—	2.632
F. Furnace ...	12.2	—	1.528	1.531	1.533	0.005	66.0	0.0	—	2.640
280560 ...	29.5	—	1.541	1.544	1.546	0.005	75.6	-9.8	—	2.762
BM 84765 ...	37.5	58.5	1.542	1.544	1.546	0.004	75.5	-18.2	—	2.789
BM 31990 ...	42.1	56.5	1.545	1.547	1.549	0.004	74.2	-22.8	—	2.807
BM 1959,359 ...	43.3	—	1.543	1.546	1.548	0.005	76.3	-23.0	—	2.837
195867 ...	45.3	37.7	1.544	1.547	1.549	0.005	68.9	-24.5	—	2.875
100446* ...	59.0	—	1.558	1.562	1.566	0.008	75.8	-39.0	—	2.959
Kasoite ...	65.5	34.6	1.564	1.568	1.572	0.008	80.0**	—	+28.0	3.001
5081 ...	85.0	—	1.580	1.583	1.586	0.006	74.1	—	+33.1	3.302
STR/5/15 ...	84.8	—	1.589	1.593	1.598	0.009	94.8	—	+32.3	3.329
10062 ...	91.9	—	1.586	1.592	1.597	0.011	87.6	—	+23.5	3.351
STR/4 ...	94.0	7.9	1.583	1.589	1.593	0.010	88.2	—	+25.7	3.347
331038 ...	97.2	2.7	1.586	1.590	1.596	0.010	93.1	—	+28.4	3.369
BM 1958,284 ...	97.8	4.4	1.585	1.589	1.595	0.010	93.2	—	+26.2	3.377
1920 ...	97.7	1.6	1.589	1.593	1.599	0.010	95.9	—	+25.1	3.378
After Vermaas (1953)										
	10.0	—	1.525	1.530	1.532	0.007	62.0	—	—	—
	50.0	—	1.555	1.562	1.564	0.009	43.0	—	—	—
	55.0	—	1.565	1.572	1.574	0.009	40.0	—	—	—
	94.0	—	1.593	1.599	1.608	0.015	95.0	—	—	—
After Segnit (1946)										
	92.2	—	1.572	—	1.584	0.012	76.0	—	29.0	—
	95.0	—	1.579	1.583	1.588	0.009	88.0	—	28.0	—
	97.0	—	1.584	1.589	1.594	0.010	93.6	—	28.0	—
After Yosimura (1939)										
Hyal. C ...	18.5	69.8	1.538	1.542	1.545	0.007	75.0	—	—	2.78
Hyal. A ...	23.5	—	1.538	1.543	1.546	0.008	75.5	-5.0	—	2.78

\* This specimen, recently collected from Japan, has kindly been supplied by Dr. S. O. Agrell.

\*\* After Yosimura (1939).

† Probable error in the refractive index value is  $\pm 0.002$ .

‡ These are the mean values as determined with the spindle stage and on a universal stage (after refraction correction) on the same grains.

The *optic axial angle* for each grain was measured independently with the spindle-stage and on the universal stage, with consistent results; the values so obtained may therefore be regarded as having been established with some degree of accuracy. Unfortunately, the variation diagram constructed from these values is most erratic, and although a tentative curve has been drawn through the points, the scatter is most disappointing. This curve is not, at present, very useful for the purpose of determining the composition since the structural state, a knowledge of

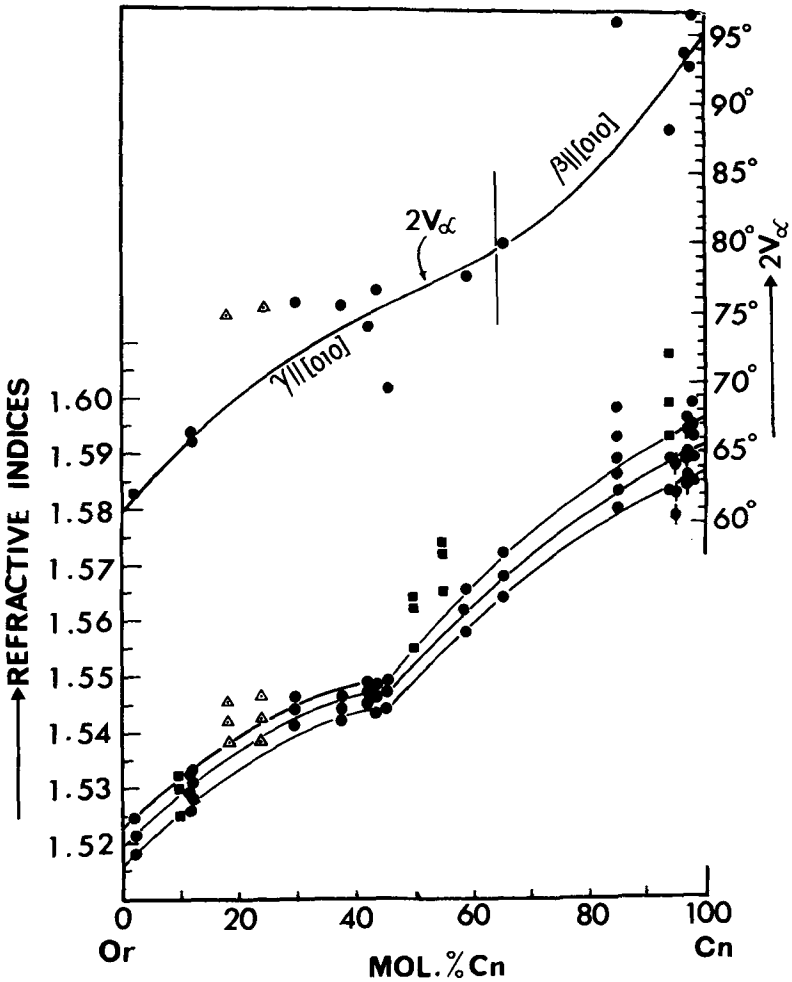


FIG. 1. Variation diagrams for the principal refractive indices and the optic axial angles for the natural specimens. ■—after Vermaas (1953); ◐—after Segnit (1946); △—after Yosimura (1939).

which is essential for this purpose in other feldspar series, is not known. The optic sign remains negative up to 65 % Cn, but for more barium-rich materials becomes positive or negative in an erratic manner.

However, neither the  $2V$  nor the refractive index diagrams shown in fig. 1 illustrate the change in optic orientation that takes place at about

65–70 % Cn (marked by a vertical line on the plot in fig. 1). This important feature of the optical properties is more apparent from extinction angle measurements.

*Variation of extinction angles.* For potassium-rich members of the series, the optic orientation is such that the obtuse bisectrix  $\gamma$  is parallel to [010]. Increased barium-content causes a rotation of the indicatrix about [010] so that the  $\beta$ -vibration direction becomes more nearly perpendicular to [001]; but before such a condition is reached, the optic orientation is completely changed at about 65–70 % Cn.

In the second orientation for the more barium-rich specimens the optic axial plane is parallel to (010), with  $\beta$  parallel to [010]. The existence of two different optic orientations is shown quite clearly from the extinction angles (table 1 and fig. 2).

Fig. 2 shows the variation of the extinction angles  $\alpha$ : [100] and  $\gamma$ : [100]. When  $\gamma \parallel$  [010], the extinction angle at first decreases slowly from small positive values at low celsian-content, but then increases sharply from zero to about  $-40^\circ$  from about 15 % Cn to 65–70 % Cn where the change in orientation takes place. Now with  $\beta \parallel$  [010], the extinction angles, although scattered, appear to show a slight decrease from about  $+30^\circ$  with increasing barium-content. Points extrapolated from the work of Tuttle (1952) for orthoclases are shown in fig. 2 (a straight line in bottom left hand), and these show a slope consistent with the present observations.

The extinction angle diagram has purposely been divided into two parts because the  $\alpha$ : [100] curve up to 60–65 % Cn may be used for determinative purposes as accurate values are easy to obtain; plotting of  $\gamma$ : [100] in terms of  $\alpha$ : [100] would have unnecessarily reduced the scale of this part of the curve which is much more precise than that determined in the region beyond 80 % Cn. In addition, there is a pronounced lack of natural specimens available in the region 65 % Cn to 80 % Cn and since 2V does not appear to pass through  $0^\circ$  between the two orientations, it is by no means certain that the extinction angle curve for  $\alpha$ : [100] is continuous within this range of composition. Winchell's diagram, extrapolated by Yosimura, implies that 2V curve would pass through  $0^\circ$  at about 65–70 % Cn. This contradicts the author's theoretical calculation (assuming the linear curves for  $\alpha$ ,  $\beta$ , and  $\gamma$  do not intersect) in which it is found that the 2V curve passes through  $90^\circ$  at about 65–70 % Cn. This in turn agrees well with the experimental data as obtained by Yosimura (1939). Fig. 3 shows the diagrams for 2V as suggested by the author, Winchell, and Yosimura after Winchell.

Winchell's extinction angle curve and Yosimura's extrapolation of it are roughly consistent in trend with the author's data.

For determinative purposes, the variation of  $\alpha$ : $[100]$  up to 60-65 %

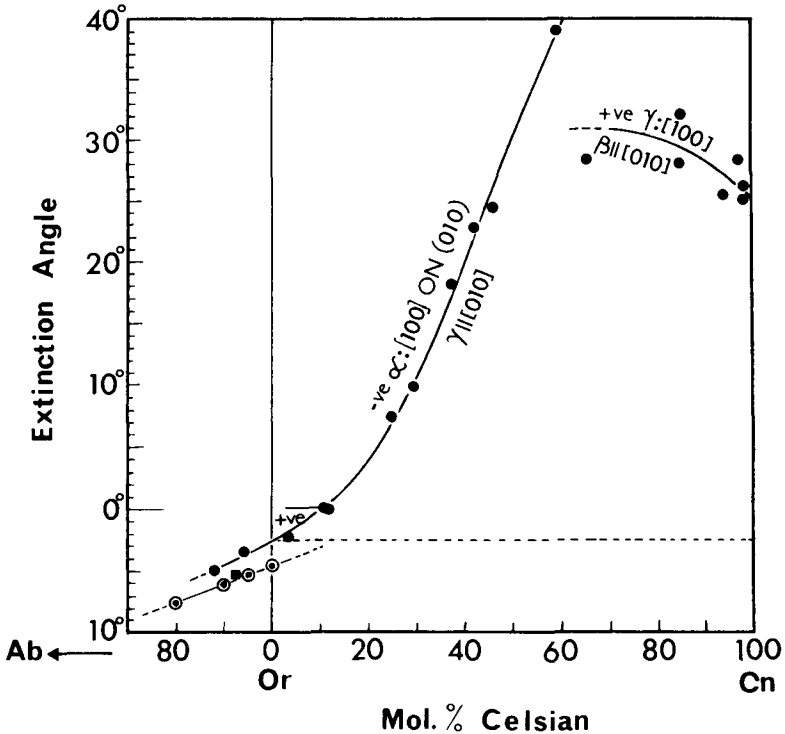


FIG. 2. Variation diagrams for the extinction angles  $\alpha$ : $[100]$  and  $\gamma$ : $[100]$  for the natural specimens.  $\odot$ —after Tuttle (1952) by extrapolation;  $\blacksquare$ —after Spencer (1937). (Above the zero-line of the ordinate, extinction angles  $\alpha$ : $[100]$  are -ve, below it are +ve. Extinction angles  $\gamma$ : $[100]$  are all +ve).

Cn provides a reasonable means of estimating the barium-content of the feldspar.

*Dispersion.* The variation of the principal refractive indices with wave-length was determined using an immersion method and a variable monochromator for three specimens over the series. The observations for all specimens are very similar and show anomalous dispersion—an increase in refractive index with increase in the wave-length of the light; but the total dispersion of each of the specimens is not

remarkable ( $\approx 0.018$  for pure celsian for wave-lengths from 450–650  $m\mu$ ).

The *densities* of the specimens were determined by the flotation method in Clerici solution. For a particular specimen, repetition of

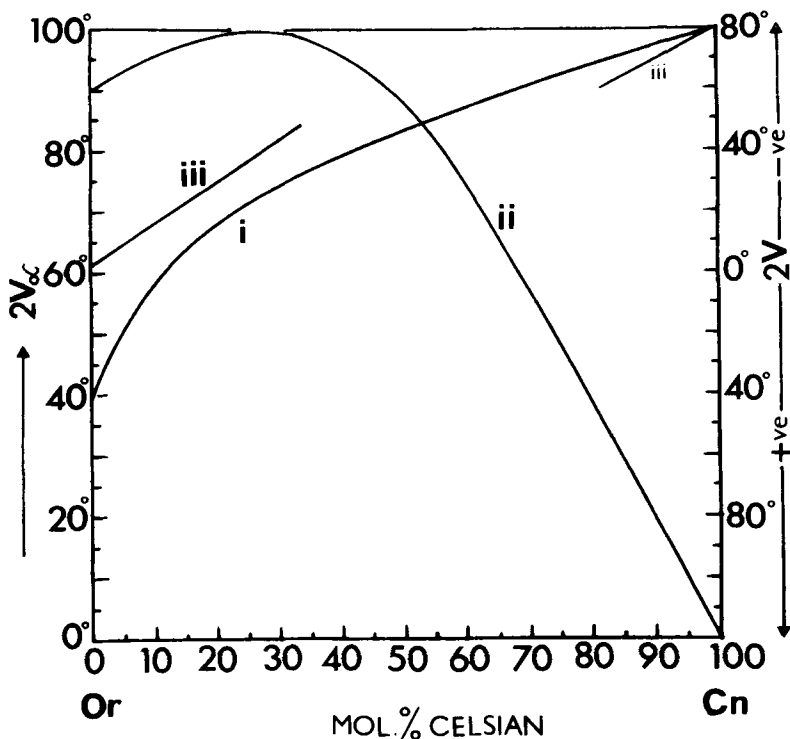


FIG. 3. Variation of  $2V$  in the orthoclase-celsian series as suggested by (i) the present author, (ii) Yosimura after Winchell, and (iii) Winchell. Note the difference in scale on the ordinate. Left-hand scale is to be used for curves (i) and (iii), right-hand scale for curve (ii).

the experiment at constant temperature ( $21 \pm 1^\circ \text{C}$ ), taking into account all probable errors but without correction for air-buoyancy, shows variation in the third decimal place, and so the accuracy has been taken as  $\pm 0.005$ .

The values obtained (table I) are plotted in fig. 5, and the variation is represented by the heavy line. The trend suggests that there is a sudden

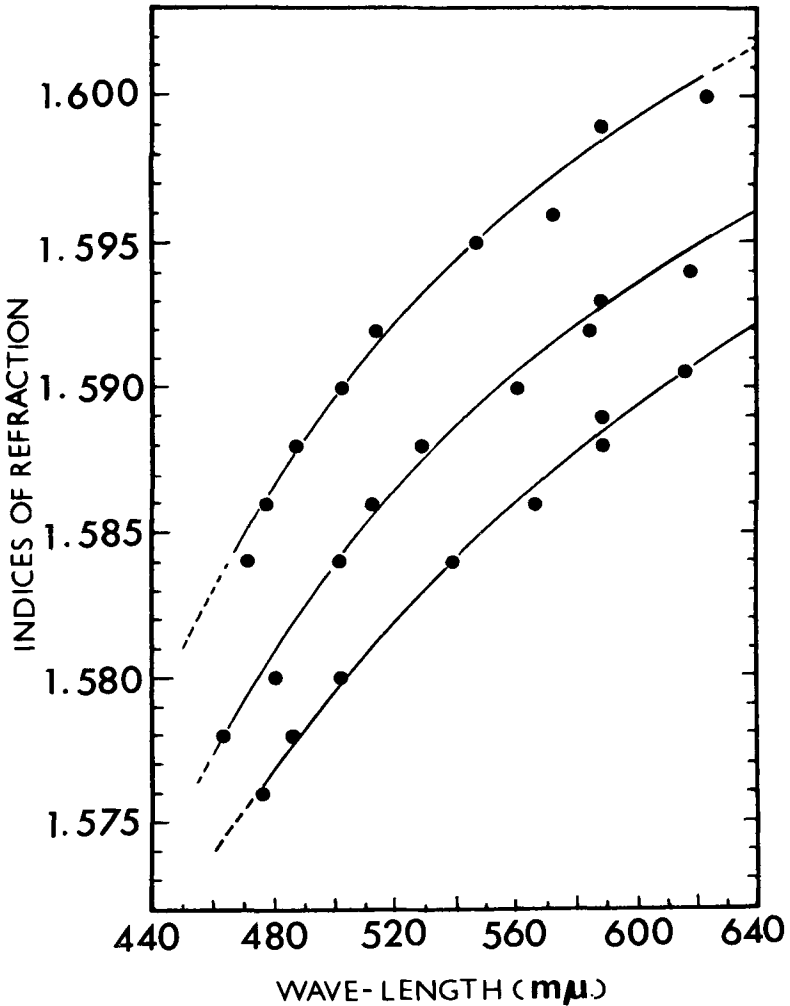


FIG. 4. Dispersion of the refractive indices of celsian (98.0 mol. % Cn).

change in the density between 60 % and 70 % Cn. The densities of synthetic specimens (described in a later paper) have been calculated from their cell-dimensions and are shown as the dotted lines. It is noteworthy that the curve for these specimens does not show the discontinuity apparent in the natural specimens.



*Discussion*

Apart from their value as determinative diagrams, the optical variation curves that have been described show two features that

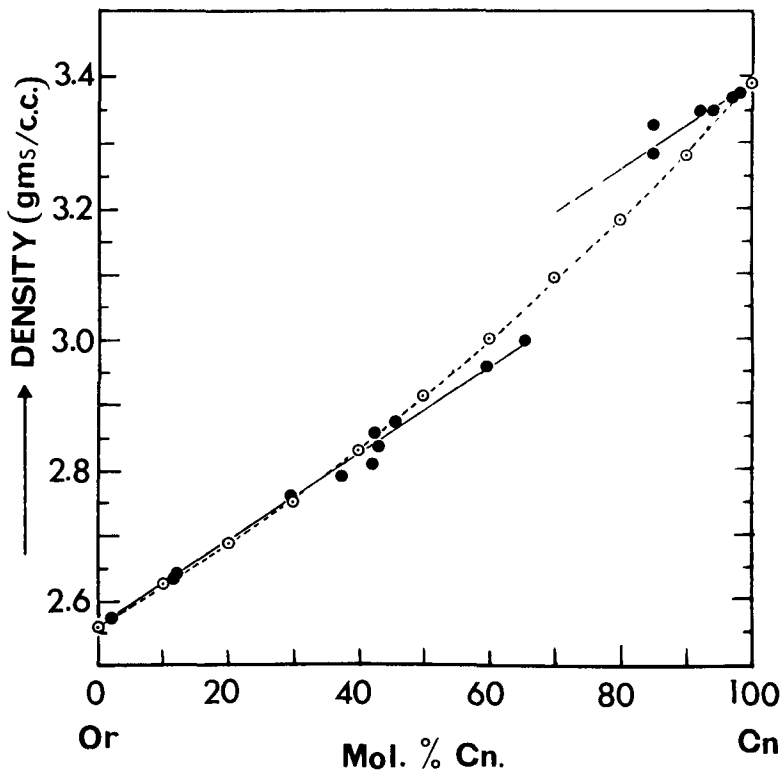


FIG. 5. Variation of densities with composition. ●—determined density for the natural specimens (solid line); ○—calculated density for the synthetic specimens (broken line).

require further comment. At about the composition of the discontinuity suggested by other authors ( $\sim 45\%$  Cn) the refractive indices apparently depart from the smooth variation that they show over the rest of the series. Such a kink in the variation is not shown by the synthetic specimens (fig. 6); its significance is not clear, and detailed comment must await further work on other specimens in this region when they are available. It may possibly be due to variation in struc-

tural state among the limited selection of specimens that has been used. Little information is available about the geological origin of most of the present specimens; with only two specimens between 50 % and 80 % Cn undue emphasis may have been given to their values.

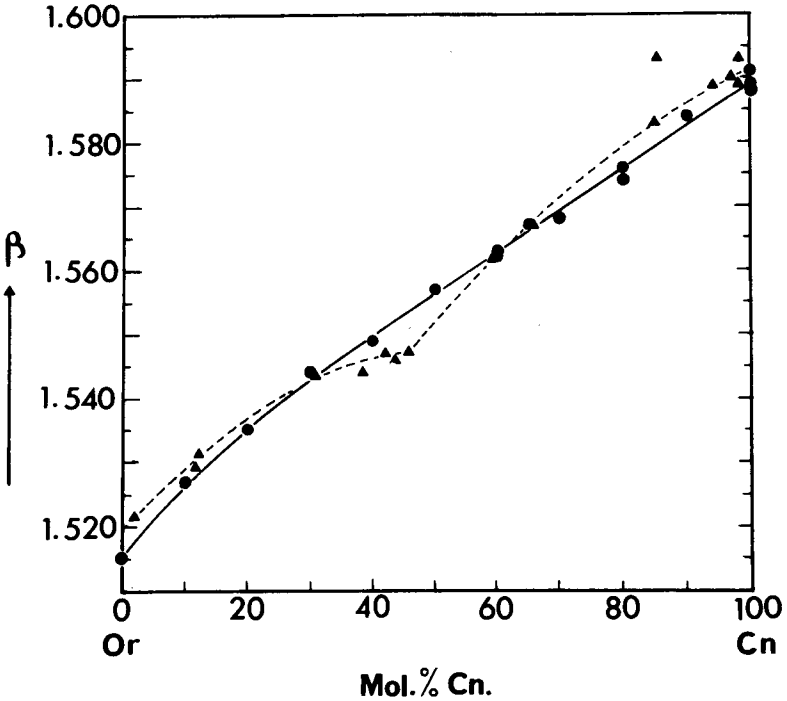


FIG. 6. Comparison of the variation of the  $\beta$ -refractive index for the natural and synthetic specimens.  $\blacktriangle$ —natural specimens, represented by a broken line;  $\bullet$ —synthetic specimens, represented by a solid line. Values for the synthetic specimens were determined at a constant temperature,  $21 \pm 1^\circ \text{C}$ .

The second notable feature is the change of optic orientation at about 65–70 % Cn, at which composition there is also a discontinuity in the density of the natural specimens. It is believed that this is of fundamental significance, for it corresponds with an important structural change. Dimensionally the monoclinic unit-cell changes very little as barium replaces potassium except that the  $c$ -axis is doubled to 14 Å for the more barium-rich members (Gay, 1956; Newnham and Megaw, 1960). It has been established by the work to be described in a later paper that the type ( $b$ ) maxima, which denote the 14 Å  $c$ -axis on electron and

X-ray diffraction patterns, are present on such single-crystal patterns only if the barium-content is equal to or greater than 70 % Cn. Moreover, from studies on synthetic crystals it is found that such maxima are not present for barium-contents up to 65 % Cn, so that the change in optic orientation and the density discontinuity seem to be associated with the occurrence of the larger cell in the more barium-rich specimens. The implication of this discontinuity will be discussed in the light of other data in a later paper.

With the exception of the optic-axial-angle variation, the curves can be used for the provisional determination of the position of a specimen within the series. It must, however, be stressed that little is known as yet of the effect of structural state upon these properties, and so such determinations must be regarded with some caution. The wide and apparently unsystematic variation in  $2V$  is probably due, at least in part, to variation in minor constituents to which the optic axial angle will be particularly sensitive.

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