Magnesium-zinc-spinels from Ceylon.

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ALTHOUGH the mineral spinel belongs to an isomorphous group, and in the simple formula $MgO.Al_2O_3$ both Mg and Al are susceptible to isomorphous replacement, yet in the transparent varieties of gem quality there is, as a rule, very little deviation from the type composition, and the physical properties are moderately constant. In fact, one may say that the only considerable replacement hitherto recorded in spinels used as gemstones is by ferrous iron in the variety known as ceylonite or pleonaste, which is black and opaque even when 7 or 8 % of FeO is present, the end-member of this series being hercynite, $FeO.Al_2O_3$, with 41 % ferrous oxide.

The purpose of this paper is to draw attention to certain transparent blue spinels from the gem gravels of Ceylon, the physical properties of which differ quite strikingly from those of the normal spinels, from which they are indistinguishable in appearance, magnesium being replaced in this instance not by ferrous iron but by zinc.

Before describing in detail the specimens of this magnesium-zinc series it will be advisable to consider the physical properties of magnesium-spinel, $MgO.Al_2O_3$, as the data in the literature are not entirely satisfactory. For instance, Rinne,[1] in his elaborate paper

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[1] F. Rinne, Neues Jahrb Min., Abt. A, 1928, Beil.-Bd. 58. p. 43. [Min. Abstr., 4–71.]

on artificial spinel, gives d 3·577 and n_D 1·7182 for the pure compound, while the following data for natural spinel are not consistent with these figures. Except for the first line, those in table I have been determined by the authors at various times.

TABLE I.   Data for ordinary gem spinels.

Colour.	Locality.	Carats.	d.	n_D.	Dispersion (6708–4227 Å.).
Crimson	India	49⅞	3·582	1·714	—[1]
Pale mauve	Burma	5·561	3·586	1·7150	0·0205
,, ,,	?	2·275	3·588	1·7152	—
Pale blue	Ceylon	—	3·584	1·7153	0·0207
Lavender	,,	3·380	3·594	1·7164	0·0206
Fine blue	,,	12·208	3·611	1·7177	0·0209
Deep indigo	,,	3·720	3·605	1·7188	0·0212

Des Cloizeaux[2] gives n_D 1·7155 for red spinel; Zimányi[3] 1·7167 for red spinel from Ceylon; Melczer[4] 1·7188 for blue spinel from Ceylon; Bauer[5] 1·7201 for blue, almost black, spinel. Schlossmacher[6] states that red, blue, brown, and violet stones from Ceylon have n_D 1·715–1·722. Church's individual values for densities range from 3·582 for red stones to 3·675 and 3·715 for indigo stones. Brauns[7] states that native spinels of all colours have densities between 3·60 and 3·62.

It would seem from the above data that pure magnesium-spinel has n_D 1·715, d 3·58, this density agreeing exactly with the theoretical density based on X-ray measurements.[8] The usual impurities, Fe, Mn, Zn, Cr, Ti, increase the values both for density and refractive index. The figures given may therefore be taken as the lower limits for natural spinel.

One or two blue spinels examined in the course of routine work had densities which seemed remarkably high, but it was not until a stone was encountered which was found to have d 3·947 and n_D 1·7432 that it became clear that there exists a variety of spinel that is quite

[1] A. H. Church, Precious Stones, London, 1905 edition, p. 68; 1924 edition, p. 85.

[2] A. Des Cloizeaux, Nouvelles recherches . . ., Mém. Acad. Sci. Paris, 1867, vol. 18, p. 203.

[3] K. Zimányi, Zeits. Kryst. Min., 1894, vol. 22, p. 328.

[4] G. Melczer, Zeits. Kryst. Min., 1900, vol. 33, p. 260.

[5] M. Bauer, Neues Jahrb. Min., 1895, vol. i, p. 281.

[6] K. Schlossmacher, Zeits. Krist., 1930, vol. 72, p. 468. [Min. Abstr., 4–255.]

[7] R. Brauns, Deutsche Goldschmiede-Zeitung, 1929, vol. 32, p. 458.

[8] S. Holgersson, Lunds Univ. Årsskrift, 1927, N.F. Avd. 2, vol. 23, no. 9.

distinct from any which has previously been recorded. The fact that the absorption spectrum of this specimen was found to be identical with that of normal blue spinel was, however, accounted sufficient evidence that no entirely new species was involved.

A diligent search amongst parcels of blue spinels from Ceylon, both as cut stones and rough water-worn pebbles, resulted in the separation of a number of specimens of this type ; the densities and refractive indices graded from 3·981 and 1·7469 down to the values for normal magnesium-spinel. For convenience of reference the data for the full range of these specimens are collected in table II. All these stones are transparent.

TABLE II.   Data for magnesium-zinc-spinels.

No.	Colour.	Density.*	n_D.†	Dispersion (6708–4227 Å.).‡	Remarks.
1.	Blue	3·981	1·7469	0·0233	—
2.	Pale blue ...	3·967	1·7465	0·0229	Analysis (p. 551)
3.	Pale lavender ...	3·947	1·7432	0·0226	4·55 cts.
4.	Dark blue-green	3·934	1·746	—	Iron rich
5.	Pale blue ...	3·904	—	—	Rough pebble
6.	Blue	3·897	1·740	—	—
7.	Sapphire-blue ...	3·885	1·739	—	—
8.	Pale lavender ...	3·883	1·7362	0·0222	Spectrum analysis
9.	,, ,, ...	3·797	1·7308	0·0218	—
10.	Indigo	3·740	1·730	—	Half of water-worn octahedron
11.	Deep indigo ...	3·733	1·7293	0·0219	—
12.	Indigo	3·712	1·7282	0·0219	—
13.	,, ...	3·690	1·7252	—	Spectrum analysis
14.	,, ...	3·635	1·7235	—	—
15.	,, ...	3·631	1·7213	0·0213	—
16.	Lavender ...	3·627	1·7196	0·0211	Spectrum analysis
17.	Deep blue-green	3·625	1·7213	—	—
18.	Pale blue ...	3·613	1·7184	0·0211	Spectrum analysis
19.	Pale indigo ...	3·606	1·7182	0·0210	—
20.	Deep ,, ...	3·605	1·7188	0·0212	Normal iron-rich type
21.	Lavender ...	3·594	1·7164	0·0206	Spectrum analysis
22.	Pale blue ...	3·584	1·7153	0·0207	—

* No. 3, ±0·001 ; other determinations ±0·003.

† No. 2, ±0·0001 ; nos. 4–7, ±0·001 ; other determinations ±0·0002 or 0·0003.

‡ All ±0·0001.

Unfortunately the specimens were not very large, the largest, no. 3, being 4·55 carats. This necessitated a special technique [1] for density

[1] H. E. Vassar, Amer. Min., 1925, vol. 10, p. 123. [M.A. 2–487.]

C. J. Payne, L. Franklin, and B. W. Anderson, Gemmologist, 1936, vol. 5, p. 274. [M.A. 6–454.]

determination by utilizing Clerici solution (thallium malonate and formate in aqueous solution), which can be readily adjusted to any given density from 4·2 downwards by dilution or concentration, the refractive index of the solution varying directly with the density. If the refractive index be measured to $\pm 0\cdot0001$, the density of the solution may be estimated to $\pm 0\cdot001$, or $\pm 0\cdot003$ allowing for experimental error.
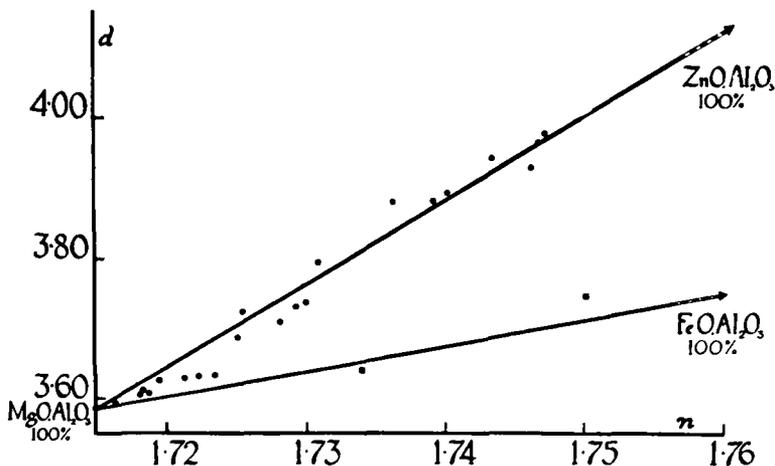

FIG. 1.   Graph plotting densities and refractive indices of magnesium-zinc-spinels (round dots) and pleonastes (square dots).

The refractive indices of all specimens were measured goniometrically by the prism method, except nos. 7 and 10.   The dispersions were measured from Li 6708 to Ca 4227 Å., the calcium line being chosen since, in conjunction with the lithium line, it gives a range corresponding roughly to that given by the solar B–G lines, and at the same time is intense, persistent, and distinctive; the shorter range, C–F (hydrogen), does not reveal such slight variation in dispersion as is shown by these specimens.   Furthermore, both these lines, together with K 7699, Tl 5350, and Ca 3934 (K), can be readily introduced into a carbon arc.   It can be seen that the dispersions vary with the refractive indices from 0·0206 to 0·0233.

It may be noted that there are slight inconsistencies in the properties shown in table II.   None of the specimens from this source is quite free from iron; many—as the colour descriptions indicate—

contain an amount of FeO quite sufficient to influence the properties. The presence of FeO causes a greater increase in refractive index relative to density than in the case of ZnO.

In fig. 1 the data given in tables I and II for n_D and d are presented graphically. It was found that when the theoretical data for the zinc-spinel, gahnite, d 4·625, n_D 1·805,[1] were plotted on this graph, the specimens under consideration occupied positions approximating very closely to a straight line drawn between the two end-members of the gahnite-spinel series. Since it could not be supposed that the replacing oxide had any influence on the colour,· it seemed very probable that the variations were due to the presence of ZnO, and the higher members of the series were, in fact, gahnite-spinels. The graph also shows a few pleonastes, which are seen to lie near a line connecting spinel to hercynite. Other replacement possibilities, considered in similar fashion, depart even farther from the steep slope leading to gahnite.

To confirm the hypothesis that the unusual properties of these spinels were due to the replacement of MgO by ZnO, a spectrographic analysis was taken of no. 8, a pale lavender stone. This was found to show strong development of the zinc lines, leaving no doubt as to the presence of a considerable quantity of this element. Traces of iron also were present, and there were traces of Mn, K, and Cu. The complete absence of all other elements, including Co, Si, Ca, Na, Cr, was noteworthy. It seems reasonable to suppose, therefore, that the colour in this specimen may be ascribed mainly to ferrous iron, possibly modified by manganese or copper.

Dr. M. H. Hey kindly undertook a quantitative micro-analysis of no. 2. a pale blue rolled pebble, in appearance indistinguishable from the normal Ceylon type. The results of the duplicate micro-analyses are as follows :

	I.	II.	Mean.	Mol. ratios.
Al_2O_3 ...	63·37	63·05	63·21	0·6201
FeO ...	1·93	1·93	1·93	0·0269 ⎫
MgO ...	16·88	16·67	16·78	0·4162 ⎬ 0·6669
ZnO ...	18·20	18·23	18·21	0·2238 ⎭
	100·38	99·88	100·13	

[1] Based on V. M. Goldschmidt's X-ray measurements of the cell side for $ZnO.Al_2O_3$, 8·062, and $MgO.Al_2O_3$, 8·059 Å. (Zeits. Physikal. Chem., Abt. B, 1932, vol. 18, p. 29), and taking the density of $MgO.Al_2O_3$ as 3·585. Refractive index as quoted by E. S. Larsen for artificial gahnite (Microscopic determination of the nonopaque minerals, Bull. U.S. Geol. Surv., 1934, no. 848, p. 58).

The iron was assumed to be in the form of FeO.[1] The analytical method used was chosen after two other possible methods had proved unsatisfactory on the micro-scale, and was as follows : 10 mg. spinel were fused with 0·15 g. $K_2S_2O_7$, dissolved, and precipitated with 8-hydroxyquinoline in alkaline tartrate solution (about N/5 NaOH). The precipitate of Zn and Mg 8-hydroxyquinolates was filtered off, dried, and weighed ; while the filtrate was neutralized with HCl, and iron and aluminium precipitated as 8-hydroxyquinolates in ammoniacal solution, filtered off, dried, and weighed. The Zn and Mg 8-hydroxyquinolates were dissolved in dilute HCl, diluted, and excess sodium acetate added so as to give a final concentration of 5 % sodium acetate and 1–2 % acetic acid ; the precipitate of zinc 8-hydroxyquinolate was filtered off, dried, and weighed. The weighed 8-hydroxyquinolates of iron and aluminium were dissolved in nitric acid, the 8-hydroxyquinoline oxidized by repeated evaporation with nitric acid and hydrogen peroxide, and iron determined colorimetrically with thioglycollic acid and ammonia. The iron determination was common to both analyses. A spectrographic analysis did not reveal the presence of any element other than those estimated above.

A calculation based on the physical data suggested that 15 % of ZnO and 18·3 % of MgO would be present, together with 0·5 % FeO, an estimate which is reasonably consistent with the percentages actually found.

With the knowledge that this specimen was destined for analysis, a 64° 7′ prism was cut and refractive indices were carefully measured for a large number of wave-lengths. The details, together with some measurements carried out on nos. 8, 9, 16, 18, 19, and 21, are given in table III.

Ultra-violet spectrograms were also prepared from fragments of nos. 13, 16, 18, and 21 in order to establish whether zinc was not present in all blue Ceylon spinels ; in all cases, except no. 17, definite evidence of this element was found. Iron was present in all the spectra, and there can be no doubt that this element is the cause of the colour, since Cr, Co, and Mn were absent. A trace of Ti was found in no. 13.

A few notes as to the absorption spectrum of blue spinel may perhaps be given here, as it is sufficiently characteristic to form a useful

[1] K. Schlossmacher and I. Meyer, Zeits. Krist., 1931, vol. 76, p. 377. [M.A. 6–265.]

diagnostic test. Wherry[1] recorded two strong bands centred at 5500 and 4600 Å., with weaker bands at 5900 and 5100. He suggested Co as the cause of all these bands, except 5100, which he ascribed to Ti.

TABLE III.   Refractive indices (± 0.0003) of magnesium-zinc-spinels for various wave-lengths.

λ.		No. 2.	No. 8.	No. 9.	No. 16.	No. 18.	No. 19.	No. 21.
7685 Å.	...	1·738	—	—	—	—	—	1·7088
6925	...	1·7412	—	—	—	—	—	1·7112
6708	...	1·7421	1·7318	1·7266	1·7154	1·7140	1·7139	1·7122
6497	...	1·7431	1·7329	—	—	—	—	1·7133
6141	...	1·7448	1·7349	—	—	—	—	1·7151
5893	...	1·7465	1·7362	1·7308	1·7196	1·7184	1·7182	1·7164
5536	...	1·7492	—	—	—	—	—	1·7188
5350	...	1·7506	1·7402	1·7346	1·7236	1·7222	1·7218	1·7200
5218	...	1·7517	1·7415	—	—	—	—	1·7213
5106	...	1·7527	1·7423	—	—	—	—	1·7221
4934	...	1·7547	1·7441	—	—	—	—	1·7240
4603	...	1·7587	1·7486	—	—	—	—	1·7283
4227	...	1·7650	1·7540	1·7484	1·7365	1·7351	1·7349	1·7328
4063	...	1·7677	—	—	—	—	—	1·7360
4023	...	1·7686	—	—	—	—	—	—
3933	...	1·7706	1·7593	1·7537	—	1·7407	—	1·7383
3883	...	1·7719	—	—	—	—	—	1·7394
Prism angle		64° 7′	51° 46′	49° 57′	62° 45¼′	63° 59¼′	63° 7¼′	62° 2¼′
Density	...	3·967	3·883	3·797	3·627	3·613	3·606	3·594

The authors' measurements on a very fine blue stone weighing 12·208 carats (see table I), using a Beck wave-length spectrometer, gave the following bands.

6320 Å. (approx.)		...	broad moderate
5920	... ...	...	weak vague
5770	... ...	...	,, ,,
5570	... ...	...	mod. weak narrow
5520	... ...	...	,, ,, ,,
5080	... ...	...	very weak narrow
4800	... ...	...	mod. strong narrow
4590	... ...	...	strong broad
4430	... ...	...	very weak narrow
4330	... ...	...	,, ,, ,,

Several of these bands cannot be observed in less richly coloured specimens, but the characteristic band at 4590 is invariably present even in pale stones, and is usually accompanied by the weaker bands at 5920, 5570, and 5520 Å.

[1] E. T. Wherry, Amer. Min., 1929, vol. 14, p. 326. [M.A. 4–209.]

In contrast to this spectrum, artificial blue spinel known to be coloured with cobalt has bands at 6330 (broad, strong), 5800 (broad, strong), 5440 (moderate, broad), 4820 (weak), 4490 (moderate, broad), 4230 (narrow, strong).

The above data, taken in conjunction with the complete absence of cobalt in all spectrum analyses undertaken, provide strong evidence that the colour and absorption bands are due not to cobalt but to ferrous iron. Schlossmacher (loc. cit.) also arrived at this conclusion from chemical analyses and a study of the absorption curves.

The hardness of the zinc-rich types is 7¾–8, as with the normal spinel. Anomalous pleochroism occurred in a few of the specimens.

While the authors have no wish to burden the literature with unnecessary names, it may be reasonably claimed that many of the specimens described depart so widely in properties and composition from the normal magnesium-spinel as to form a distinct sub-variety, more distinct, for instance, than the iron-rich 'chlorospinel'. Since 'spinel' is the group name, 'zinc-spinel' would be held merely to denote gahnite. 'Gahnospinel' is tentatively suggested.

It may be wondered why members of this sub-variety have not previously been recorded. The explanation seems to lie in their comparative rarity. Out of over 300 specimens of blue spinel from parcels of mixed Ceylon stones only four were found with densities greater than 3·85. Types with lower percentages of zinc are more common, and, in fact, it seems that zinc is rarely altogether absent from blue Ceylon spinels.