AN ARTIFICIAL GEM-STONE ISOMORPHOUS WITH SPINEL

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INTODUCTION[1]

Two crystalline types of artificial gem-stones are now manufactured on a commercial scale. From the chemical standpoint these are either alumina or magnesium-aluminate. The alumina type (artificial corundum) has been manufactured in several different colors for some time.[2] Magnesium-aluminate gem-stones, however, have only recently assumed commercial importance in the artificial gem trade.

According to Clarke the magnesium-aluminate, spinel, has been synthesized in several ways and by a number of investigators.[3] It has also been known for some time that gem material approaching spinel in character can be manufacutred. Smith[4] described artificial gem-stones which he called synthetic spinel over twenty years ago. These had the physical properties of spinel and agreed both in optical properties and system of crystallization with that mineral. No chemical analysis, however, was included in his description and it is not certain how the product corresponded with spinel.

Recently Rinne has carried out an extended study of synthetic spinel.[5] His work leaves little to be added to the subject. It seems proper, however, to give a few observations which may be of interest to readers of the *American Mineralogist*, although the work has not been carried out with the refinement accomplished by Rinne and his assistants. In view of the fact, however, that only slight attention has been paid to synthetic spinel by American writ-

[1] The artificial gem-stones studied in this investigation were kindly furnished by Mr. Milton Heller of L. Heller and Son.

[2] Verneuil, A., Memoire sur la reproduction artificielle du rubis par fusion. *Ann. d. ch. et de phys.*, S. 8, **3,** 1904, p. 20.

[3] Clarke, F. W., Data of Geochemistry, 5th ed., *Bull.* **770,** *U. S. Geol. Surv.*, 1924.

[4] Smith, G. F. Herbert, Note on synthetical corundum and spinel. *Mineral. Mag.*, **15,** 1908, p. 153.

[5] F. Rinne, Morph. u. phys.-chem. Untersuchungen an synthetischen Spinellen, etc., *Neues Jahrb. Min., Geol.,* **LVIII.** Beilage-Band. Abt. A. Erstes Heft, **1928,** pp. 43–108.

ers, it would seem that it should not be amiss to make available some independent observations on commercial material now being handled in this country.

An opportunity was recently offered the writer to examine several packets of artificial gems. The stones were of three colors, pale blue, bluish green, and rose-pink, and presented a most striking appearance. Upon examination and analysis all proved to be composed of the same substance. This substance was essentially a magnesium-aluminate isomorphous with spinel.

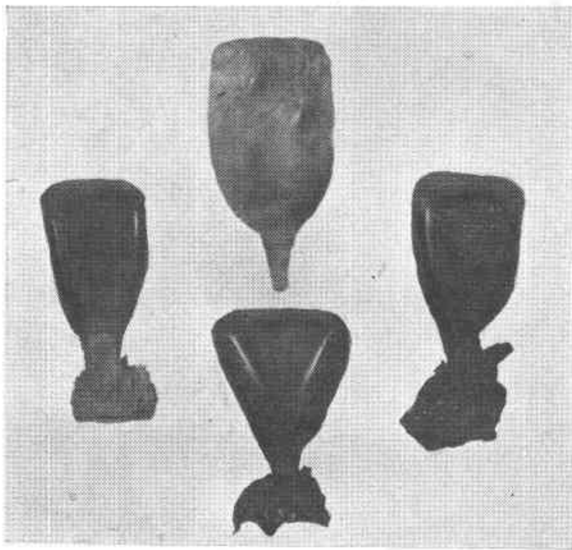

FIG. 1. "Boules" of artificial gem-stones now on the market. The three lower ones represent a magnesium-aluminate type, while the upper "boule" is synthetic corundum.

THE PROPERTIES OF THE ARTIFICIAL GEM-STONES

The stones are formed by the same blowpipe method employed in producing artificial corundum gems. The "boule," as the uncut material is called, grows upward by the addition of fused matter from the mouth of an oxy-hydrogen blowpipe mounted in a vertical position. The final product has the shape of the lower specimens shown in Figure 1. A "boule" formed of the more commonly known alumina, on the other hand, grows into a rounded, more or less pear-shaped form, as illustrated in the upper central part of the figure. The magnesium-aluminate "boules" may be well crystallized. Occasionally a crystal resembling the usual spinel twin results from the fusion. More often, however, the cross section is nearly square. Partly developed octahedral forms are common. Cubic parting is evident in some specimens, and in others the stone breaks along octahedral planes.

The hardness of the material is 8. The specific gravities of the three stones were determined as follows:

Pale blue	3.71
Bluish-green	3.57
Rose pink	3.48

The index of refration varies little from stone to stone, being very nearly N_{Na} equals 1.721. This is slightly greater than the figure given by Melczer, N_{Na} equals 1.7188 for blue spinel from Ceylon.[6] The material is in general isotropic but shows weak double refraction forming a gridlike pattern. This was noted by Michel,[7] and is given by him as a criterion for the recognition of stones which he calls "synthetic spinel." Judging from the work of those who have investigated the magnesia-alumina series,[8] the double refraction may indicate the presence of an additional Al_2O_3 phase with the phase Mg Al_2O_4. The question of this phase is taken up in detail by Rinne.[9]

The properties of these artificial gem-stones differ considerably from those of the artificial corundum gems.[10] The difference is so distinct that no occasion should arise for confusing them with the other product.

An X-Ray Study of the Gem-Stones

X-ray diffraction patterns were taken of both the pink artificial gem-stone and ruby spinel from Ceylon. These were measured and the interplanar atomic spacings computed. A comparison of the results of the two sets of computations is shown by diagram in Figure 2. The artificial product is evidently isomorphous with the Ceylon spinel, but the interplanar spacings are smaller than in the mineral.

[6] Melczer, G., Ueber einige Mineralien, vorwiegend von Ceylon. *Zeit. Krist.*, **33,** 1900, p. 259.

[7] Michel, H., The Pocketbook for Jewelers. Gustave Herz, *New York,* **1928.**

[8] Rankin, G. A., and Merwin, H. E., The Ternary System $CaO-Al_2O_3-MgO$, *Journ. Amer. Chem. Soc.*, **38,** 1916, p. 571.

[9] *Loc. cit.*

[10] Moses, A. J., Some Tests upon the Synthetic Sapphires of Verneuil. *Amer. Journ. Sci.*, **30,** 1910, p. 271.

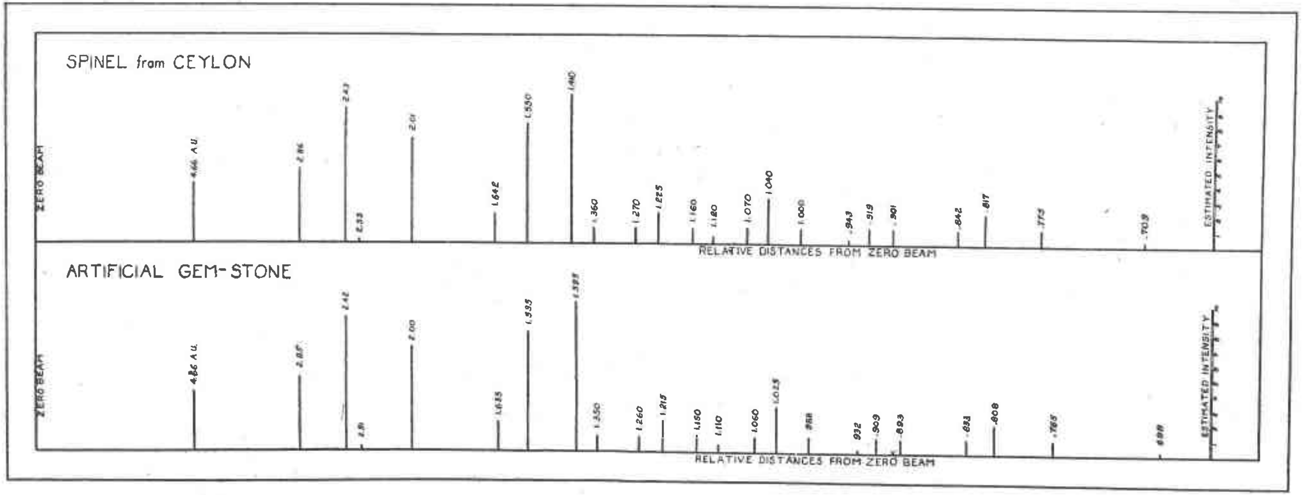

Fig. 2 Diagram giving the relative interplanar atomic spacing of Ceylon spinel and the artificial gem-stone of the spinel type. The lines show the relative distance from the zero beam as measured on an X-ray diffraction pattern, the estimated intensity of lines, and the interplanar atomic spacing in Ångstrom units.

The crystal structure of the spinel group has been investigated by Bragg,[11] Nishikawa,[12] and Goldschmidt.[13] These authors agree in assigning the diamond type of lattice to the group and the spinel structure which they determined has since become a standard type. The spinel mineral examined by Nishikawa was ruby spinel from Ceylon. Judging from the description it was of the same type as that used for comparison in Figure 2. It may be assumed, therefore, that the diffraction pattern of the Ceylon material is that to be expected from a crystal having the diamond type of lattice and the atomic arrangement of spinel. The artificial product would also be made up of atoms arranged according to the "spinel type" of structure. In the latter case, however, the interplanar spacing is less. Computation of the Miller indices of the lines given by the artificial stone according to the method of Hull,[14] shows the material to have the generally recognized "spinel type" of structure. Posnjak,[15] has worked out the lattice dimensions of spinel by means of X-ray diffraction patterns and has given detailed measurements.

According to Bragg, the distance $2d$ (100) for magnetite is 4.15 Å. U. In the case of the Ceylon spinel shown in Figure 2, the distance $2d_{100}$ is 4.02 Å. U. and the same spacing for the artificial gem-stones is 4.00 Å. U. The difference between 4.00 Å. U. and 4.15 Å. U. probably very nearly represents the range of $2d_{100}$ for the spinel group, for in other X-ray work it has been shown that [16] franklinite is at least close to magnetite and possibly the same, while chromite lies between magnetite and spinel.

Chemical Analysis

The magnesia content of the three samples tested was shown by analysis to be too low for ruby spinel.[17] The alumina content was

[11] Bragg, W. H., The structure of the Spinel Group of Crystals. *Phil. Mag.* **30**, 1915. p. 305.

[12] Nishikawa, S., *Proc. Tokyo Math. Phys. Soc.*, **8**, 1915–16, p. 199.

[13] V. M. Goldschmidt, T. Barth u. G. Lunde, *Norsk Vidensk.-Akad.*, Oslo, Mat.-naturv. Kl., **1925**, N. F. I.

[14] Hull, A. W., A New Method of X-ray Crystal Analysis, *Phys. Rev.*, **10**, 1917, p. 661.

[15] Posnjak, E., *Amer. J. Sci.*, Ser. 5, vol. **XVI**, 1928, p. 528.

[16] Kerr, Paul F., The determination of opaque ore-minerals by X-ray diffraction patterns. *Econ. Geol.*, **19**, 1924, p. 1.

[17] All of the chemical work was carried on by Ledoux & Co., New York, under the supervision of Mr. A. M. Smoot.

correspondingly too high. The results of the two partial analyses and a portion of a complete analysis of the rose-pink colored stone are as follows:

	Rose-pink Stone	Bluish-green Stone	Blue Stone
Alumina (Al_2O_3)	87.50%	89.17%	88.95%
Magnesia (MgO)	10.66%	9.69%	9.70%
		98.86%	98.65%

Crystals of pale ruby spinel from Ceylon were carefully selected and submitted for a complete analysis, to be compared with a complete analysis of the rose-pink artificial stone. The results of these two analyses are given below:

	Ruby Spinel from Ceylon	Rose-pink Artificial Gem-Stone
Alumina (Al_2O_3)	70.00 per cent	87.50 per cent
Magnesia (MgO)	28.10 " "	10.66 " "
Calcium oxide (CaO)	0.06 " "	0.06 " "
Ferrous oxide (FeO)	0.45 " "	0.82 " "
Chromic oxide (Cr_2O_3)	0.39 " "	not found
Silica (SiO_2)	0.74 " "	0.62 " "
Titanium oxide (TiO_2)	0.10 " "	not found
Manganese oxide (MnO)	trace	trace
	99.84 per cent	99.66 per cent

The analysis of the spinel from Ceylon agrees closely with other analyses of spinel from the same locality already on record. It is also not far from the theoretical composition of spinel. The magnesia and alumina content of the rose-pink artificial gem-stone, however, differ considerably from spinel. The material, therefore, is properly a synthetic isomorph of spinel.

Conclusion

The artificial gem-stones, as has been previously recognized, have the crystal structure of spinel. The atomic spacing based on X-ray patterns, however, is $2d_{100}$ 4.00 Å. U., instead of $2d_{100}$ 4.02 Å. U. as in the case of ruby spinel. The magnesia content of the material is also much too low to agree with ruby spinel, while the alumina on the other hand is correspondingly high. The optical and physical properties, however, agree closely with those of spinel, and it is, therefore, concluded that the material is a synthetic isomorph of spinel. Rinne has shown, however, that synthetic spinel with the correct magnesia-alumina ratio can be manufactured.