THE WURTZITE-GREENOCKITE SERIES*

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Abstract

Specimens from Tsumeb, Southwest Africa, are found to be intermediate members in the wurtzite-greenockite series. Green, brown and orange color varieties are described that have respectively Cd:Zn ratios: 41.5:58.4; 54.2:45.8; 57.6:42.4. A linear variation is shown from wurtzite to greenockite in specific gravity, refractive indices, and unit cell dimensions. All varieties fluoresce in the U.V. As in synthetic phosphors the peak of the luminescent band is displaced from blue toward red with increasing cadmium.

Introduction

The few available analyses of greenockite and wurtzite show for both minerals only slight variations from the theoretical compositions. Very little solid solution between the two minerals has been reported in spite of the fact that a complete series has been synthesized.

Through the kindness of Dr. G. Söhnge and Dr. B. H. Geier of the Tsumeb Corporation, several specimens from Tsumeb, Southwest Africa, containing minerals that carry appreciable amounts of both zinc and cadmium, were made available for study. These proved to be intermediate members in the wurtzite-greenockite series. On the basis of color the minerals can be separated into three distinct varieties: 1. orange, 2. brown, 3. green.

Occurrence†

The zinc-cadmium sulfides were found mainly in the 1940 and 1941 stopes near the west end of the steeply plunging pipe-like Tsumeb ore body between the 17 (1595 ft.) and 20 (1890 ft.) levels. The minerals showed up in noteworthy concentrations in the footwall portion of the main lens of high-grade ore that was about 30 feet wide. Assays from this particular zone averaged 13 per cent cadmium as compared with an average of 0.2 per cent in the mill heads of run-of-mine ore. The Zn-Cd sulfides were scattered through a lead-rich, zinc-deficient mineral assemblage containing moderate amounts of pyrite, tennantite, bornite, chalcocite and digenite. The orange variety showed a marked concentration in chert and shale, the brown variety mostly in pseudo-aplite, whereas no special preference was evident in the green variety. In order of abundance the brown sulfide predominated, the orange being subordinate,

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† This statement of *occurrence* supplied by G. Söhnge.

whereas the green variety occurred only sporadically; all three, however, were closely associated within the cadmium bearing zone which appeared to have escaped supergene effects.

CHEMISTRY

Although adequate amounts of the brown and green varieties were available, they both were so intimately mixed with other minerals, notably quartz, galena and pyrite, that it was impossible to separate a sample sufficient for chemical analysis that was free from impurities. Specimens containing these minerals were finely crushed and sizes minus 325–plus 400 mesh were separated. Initial separations were made using methylene iodide to remove fragments with specific gravity less than 3.30. The heavier portions were then separated with a Frantz *isodynamic separator*. Microscopic examination showed that, even with many passings through the separator, the majority of the grains had minute specks of impurities attached to them. Chemical analyses were made, therefore, on samples in which it was recognized that there were small amounts of galena, pyrite and quartz. Spectrographic analyses of a few milligrams of carefully hand-picked material free from visible impurities showed for all varieties the presence of copper and manganese

TABLE 1. CHEMICAL ANALYSES OF CD-ZN MINERALS, TSUMEB

	Green		Brown		Orange
	1	1*a*	2	2*a*	3
Cd	31.93	39.87	43.66	49.34	49.75
Zn	25.92	32.36	21.48	24.27	21.30
Ca	0.65	0.81	1.35	1.53	tr.
Mn	0.34	0.43	0.61	0.69	0.12
Pb	9.09		1.96		none
Fe	1.51		2.97		none
S	24.39	26.53	25.10	24.17	
Insol.	5.94		3.33		0.65
	99.77	100.00	100.46	100.00	
Atomic proportions Cd:Zn	41.5:58.4		54.2:45.8		57.6:42.4
Specific Gravity					
Meas.				4.50	4.53
Calc.		4.44		4.53	4.54

Chemical analyses by Jun Ito.

Analyses 1*a* and 2*a* recalculated to 100 per cent after removing Pb, Fe and sulfur for PbS and FeS_2.

but the absence of iron and lead. One seemed justified, therefore, in considering the iron and lead reported in the chemical analyses as due to the presence of pyrite and galena and that manganese and copper substitute for zinc or cadmium in the structure. The insoluble portion was considered to be quartz.

Although the orange variety was extremely limited, it was sufficiently coarse so that it was possible to hand pick 140 milligrams of the mineral free from impurities. On this small amount of material only the metallic elements could be determined.

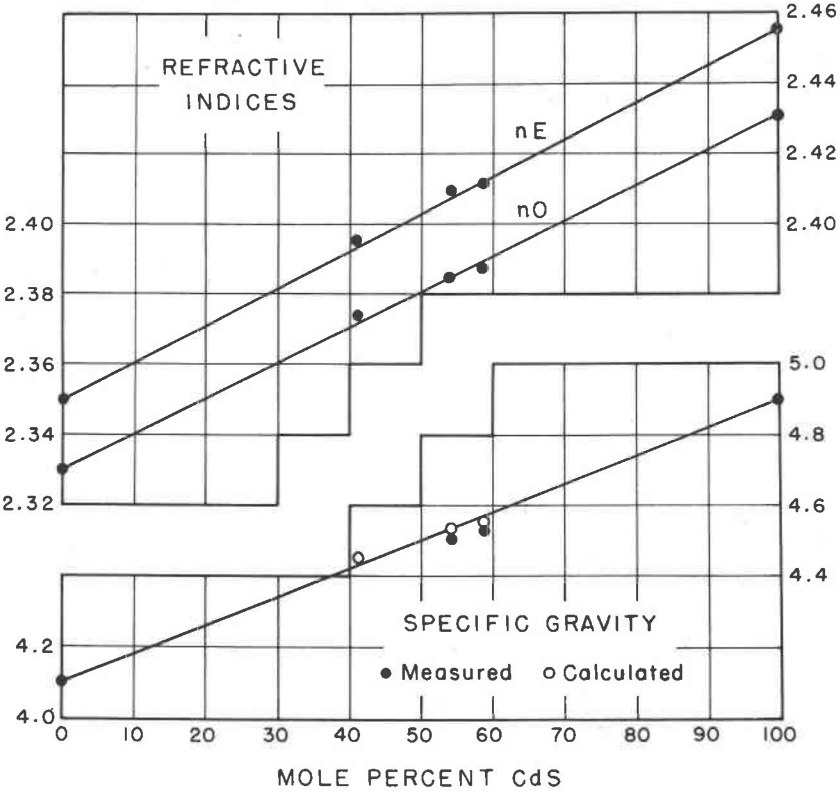

FIG. 1. Refractive indices and specific gravity, wurtzite-greenockite series.

PHYSICAL PROPERTIES

Both the orange and brown varieties show poor $\{11\bar{2}0\}$ and $\{0001\}$ cleavage, the same as reported for wurtzite. In addition, the orange variety also shows evidence of a poor $\{11\bar{2}2\}$ cleavage. No cleavage was observed on the green variety but because of the fine-grained nature of the material, this should not be considered as evidence of the lack of cleavage.

The specific gravities of the orange and brown varieties were determined on the Berman balance, using carefully hand-picked material. The specific gravities are: on 25 milligrams of the orange variety, 4.53; on 9 milligrams of the brown variety, 4.50. These values are plotted in Fig. 1 with the measured values of the specific gravity of wurtzite (4.1) and greenockite (4.9). Assuming that the change in specific gravity with composition is linear, the measured values given above should fall on the straight line. Both fall slightly below. The calculated values for the specific gravity are green variety, 4.44; brown variety, 4.53; orange variety, 4.54.

Optical Properties

Wurtzite, greenockite and the intermediate members in the series are all uniaxial positive. The refractive indices given in Table 2 vary with the composition as shown in Fig. 1. Refractive indices for wurtzite and greenockite are from Vol. 1, *System of Mineralogy* (1944); the others as reported are ±0.003.

TABLE 2. REFRACTIVE INDICES. WURTZITE-GREENOCKITE SERIES

	Wurtzite	41.5 CdS	54.2 CdS	57.6 CdS	Greenockite
nO_{Li}	2.330	2.374	2.382	2.388	2.431
nE_{Li}	2.350	2.395	2.405	2.409	2.456

Fluorescence

The literature on the fluorescence of the synthetic zinc-cadmium sulfide solid solution series is voluminous. Most of it is summarized in the books by Leverenz (1950) and Fonda and Seitz (1948). This solid solution series is of particular interest because of its use in the preparation of commercial phosphors. These are usually prepared, according to Kroger and Dikhoff (1950), by heating together pure ZnS and CdS with a small amount of an activator (Ag, Cu, Au, Mn) and a halide. The monovalent Ag^+, Cu^+, Au^+ substitute for the Zn^{++}. The halide serves a dual purpose. It acts as a flux and enters into the structure as anions Cl^-, Br^-, or I^- forming a coupled substitution. In this solid solution series the peak of the luminescent band is displaced from the blue toward the red end of the spectrum with increasing cadmium concentration.

In the minerals under consideration, the same phenomenon is observed as in the synthetic material. The fluorescent colors of the three members of the series are as follows:

Color of Mineral	Mole per cent CdS	Fluorescent Color
orange	57.6	orange-red
brown	54.2	yellow-orange
green	41.5	yellow

In an examination in ultra-violet light of 34 wurtzite and 42 greenockite specimens in the Harvard collection, no fluorescence was shown by any of them. This lack of fluorescence probably indicates, as do chemical analyses of greenockite and wurtzite, that there is normally little if any solid solution. Schroll (1953) in a study of the trace elements in wurtzite and sphalerite points out that the maximum amount of cadmium reported in wurtzite is three per cent and is normally less than one per cent.

UNIT CELL

X-ray powder photographs of the three varieties were indexed and from these the unit cell dimensions given below were calculated. Rotation and Weissenberg photographs were also taken of the brown variety, rotating the crystal about both the *c* and *a* axes. The 0-layer Weissenberg photograph taken about the *a* axis was carefully inspected for evidence of a multiple cell along *c* as described by Frondel and Palache (1950) for polymorphs of wurtzite. None was found and the structure is that of wurtzite 2H in the designation proposed by Ramsdell (1947) for silicon carbide.

The systematic extinctions shown on the single crystal photographs lead to the space groups *C6/mmc* or *C6mc*. No crystal forms are present to aid in determining the symmetry but a strong piezoelectric response shows the space group to be *C6mc*, the same as in wurtzite and greenockite.

TABLE 3. UNIT CELL DIMENSIONS. WURTZITE-GREENOCKITE SERIES

	Wurtzite	Green var.	Brown var.	Orange var.	Greenockite
a_0	3.811 Å	3.958	3.995	4.006	4.142
c_0	6.234 Å	6.444	6.490	6.510	6.724

The unit cell dimensions of the series show a systematic change from wurtzite to greenockite, and, as in the other properties, vary almost linearly as shown in Fig. 2.

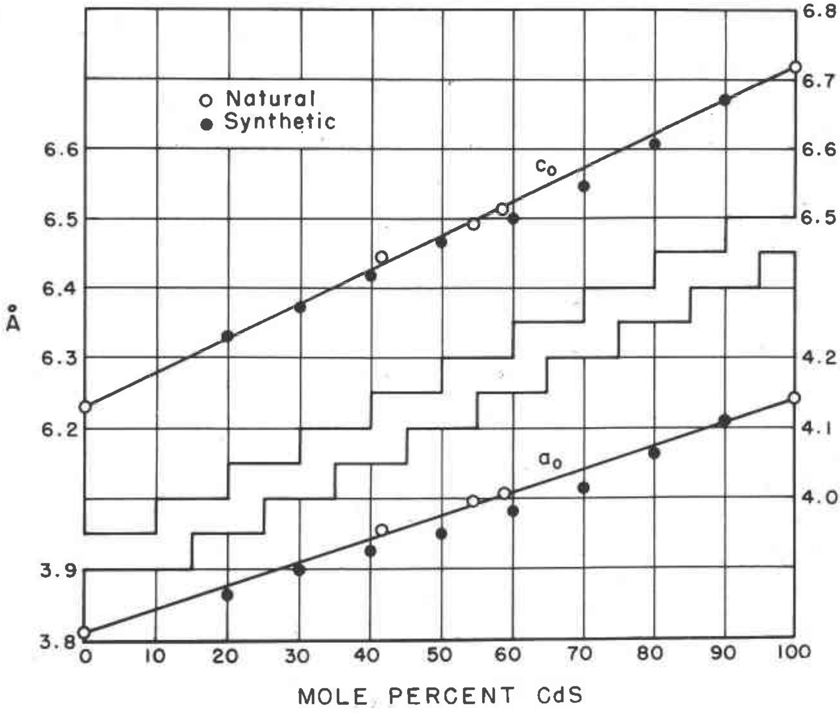

FIG. 2. Unit cell dimensions, wurtzite-greenockite series.

A series of zinc-cadmium phosphors synthesized by Dr. E. S. Rittner were available for study and comparison with the natural material. The dimensions of the unit cells of this series depart more from linearity than do those of the natural minerals as shown in Fig. 2.

TABLE 4. UNIT CELL DIMENSIONS. SYNTHESIZED ZINC-CADMIUM SULFIDES

Per cent CdS	20	30	40	50	60	70	80	90	100
a_0	3.863 Å	3.898	3.922	3.950	3.979	4.012	4.063	4.098	4.143
c_0	6.329 Å	6.373	6.418	6.464	6.498	6.545	6.604	6.677	6.729

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