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COLOUR OF SPHALERITE

by

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(with 7 text-figures and 3 tables)

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Abstract

The colour of sphalerite is white nearly colourless when pure, whereas sphalerite with high Fe content is almost black in colour. Besides a minor amount of cadmium and manganese is contained in addition to iron. The present writer has carried out some quantitative studies on the colour of sphalerite, especially in connection between the chemical components and whiteness. The whiteness in colour of sphalerite in which Fe ion substituting for Zn ion, decreases from 72% to 12% straightly, as the Fe content increases from 0% to 15%.

Introduction

The colour of sphalerite is white to nearly colourless when pure, but this occurs only very seldom in nature. The colourless sphalerite from the Hosokura mine, Miyagi Prefecture is the sole occurrence in Japan and was reported by the author (Togari 1961), unfortunately there is no move colourless sphalerite in this mine. Besides the colour of sphalerite shows commonly brown, yellow, black, and also red and green. The colourless sphalerite used in this work is the synthetic material made in quartz tube under high temperature and 1 atmosphere. Colour of Japanese sphalerite varies in wide range among which yellow is most common, and black comes next. The other colours noticed comprise green, orange, and red, which may be pale or deep, and light or dark. Blue, violet and purple sphalerites have never been absent. (Togari, 1954, 1958, 1959).

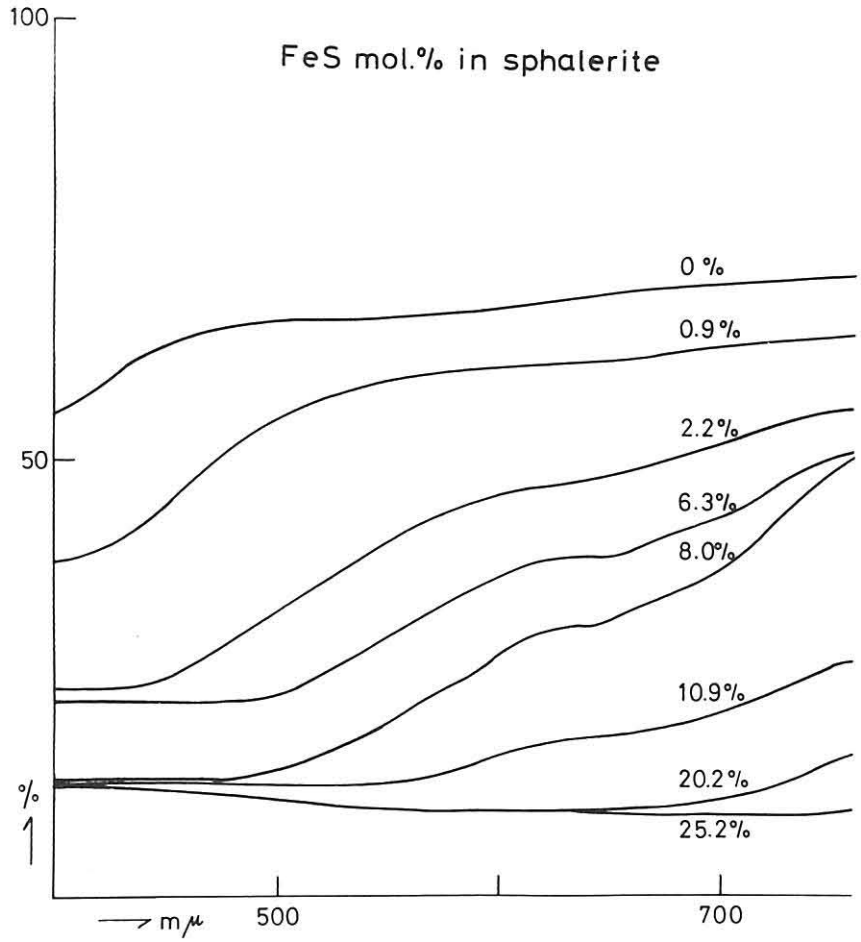
Three subordinative properties in colour consist of lightness, hue and saturation, which vary independently to each other. In the previous paper (Togari 1961) it was pointed out that colouring of sphalerite is caused by its peculiar property of semiconductance and that variable chromaticity in colour is due to the presence of excess sulphur over metal ions.

From the viewpoint above mentioned, the quantitative analysis of sphalerite colour was made by means of a photoelectric-spectro reflect meter and trichromatic specification was determined by the CIE (Commission

Internationale de l'Eclairage) chromaticity diagram.

Experimental methods and samples

Experimental study on the subordinate properties of colour in sphalerite has never been made so far. The trichromatic specification through the photo-electric-spectrometer is the best method for such studies (Hunter 1958). However, since this apparatus was not available in the writer's laboratory,



Text-Fig. 1 Spectroscopic reflectivity of sphalerite in which the Fe ion substitutes for position of Zn ion in crystal structure. Numbers above each curve show FeS mol. % in sphalerite.
Abscissa: percent of reflectance relative to working standard (Al_2O_3).
Ordinate: wave length measured by spectroscopic reflectmeter ($m\mu$).

quantitative analysis of sphalerite colour was determined by Ostwald's standard colour table as mentioned in his previous papers (Togari 1954, 1958, 1959, 1961). In the present experiment an automatic photoelectric spectro reflectmeter for colorimetry was used.

Spectroscopic reflective curve of sphalerite samples arranged in the order of grain size from 0.1 mm to 0.25 mm, was obtained by the equipment above mentioned. Then the tristmulus values are calculated from above mentioned curve through the trichromatic integrator by selected ordinate method (Azuma 1947). From the trichromatic coefficients calculated upon those values, the trichromatic subordinative properties (lightness, hue and saturation) are determined by CIE chromaticity diagram.

The lightness value and saturation value are shown in percentage, whereas the hue is given in dominant wavelength.

The sphalerite samples for this experiments were mainly the minerals from the Hosokura mine, Miyagi Prefecture and the Toyoha mine, Hokkaido, and partially synthetic materials were also used.

Experimental results

Various influences by FeS molecules substituting for sphalerite

Spectroscopic reflective curve of sphalerite in which the Fe ion substitutes for position of Zn ion on crystal structure was measured by the automatic photoelectric spectro-reflectmeter. These spectral curves for colourimetry are shown in Text-Fig. 1.

Table 1 Trichromatic coefficients of sphalerite in which the Fe ion substitutes for Zn ion.

FeS%	Y(%)	Pe (%)	W (%)	λ (mμ)
0	66.6	3.2	66.4	colourless
0.88	58.6	14.0	56.3	572 (gr. yel.)
1.16	53.8	30.0	47.6	580 (yel.)
2.15	39.7	25.8	34.5	578 (yel.)
4.00	31.8	26.4	25.8	585 (yel. or.)
6.30	23.1	27.7	18.7	585 (yel. or.)
8.00	18.6	32.0	12.8	586 (yel. or.)
10.88	13.6	8.0	13.5	
15.24	12.2	5.4	11.9	
20.21	10.1	8.4	9.7	
25.19	10.0	9.2	9.8	
30.17	9.7	9.4	9.3	

Y(%): lightness in trichromatic coefficients, Pe (%): saturation, (mμ): hue, W (%): whiteness, gr. yel.: greenish yellow, yel.: yellow, yel. or.: yellowish orange.

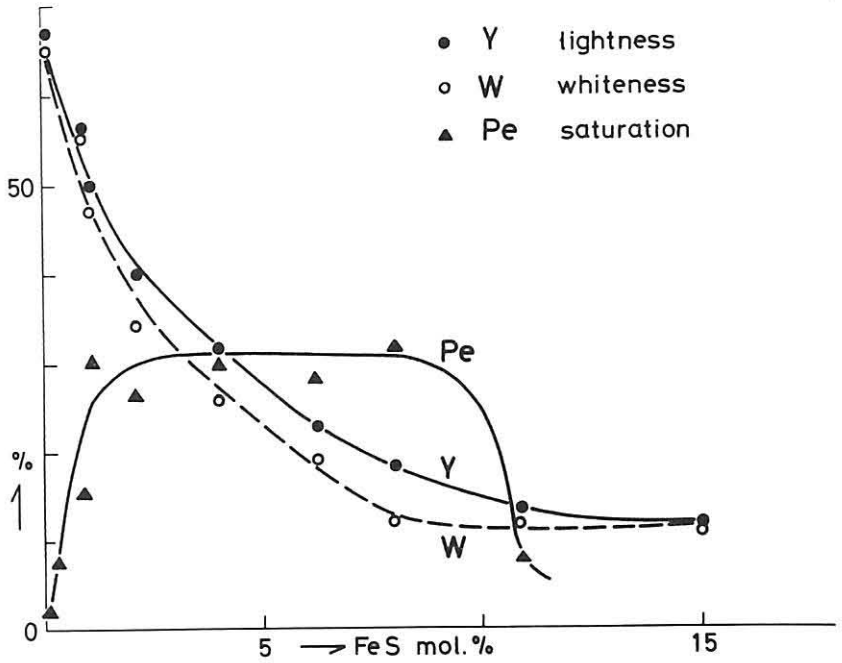
The trichromatic subordinate properties measured and calculated from spectral curves are collected in Table 1. Whiteness not being the trichromatic subordinate properties is calculated by the Hunter equation, $W=100-\sqrt{(100-Y)^2+Pe^2}$ (Hunter 1958). Therefore whiteness value is always smaller than lightness one without colourless sample. In Table 1, it is pointed out that the dominant wave length for hue in colour is almost invariable, but that it changes slightly toward long wave length with increasing Fe content.

Trichromatic specification diagram determined by CIE chromaticity diagram are shown in Text-Fig. 2, which shervs that both lightness and whiteness decrease along logarithm curved line with the increase in FeS mol. percent.

The influence of FeS content upon the whiteness is distinct, when it is less than 2% and its whiteness value amounts to 30% for maximum one.

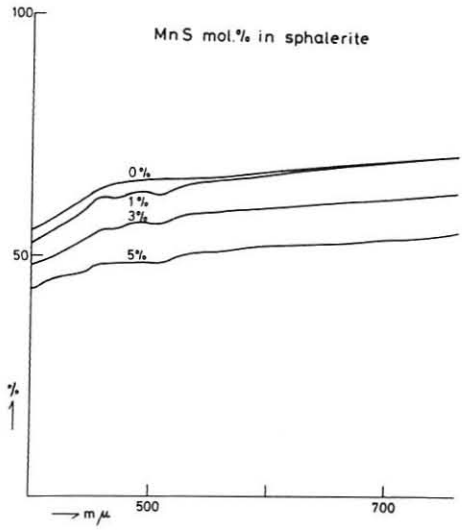
Influences of MnS and CdS molecules substituting for sphalerite

Spectroscopic reflective curves of sphalerite in which the Mn or Cd ions substitute for Zn ions are shown in Text-Figs. 3 and 4. Their trichromatic subordinate properties and their whiteness are given in Tables 2 and 3, and trichromatic specification is shown diagrammatically in Text-Figs. 5 and 6.

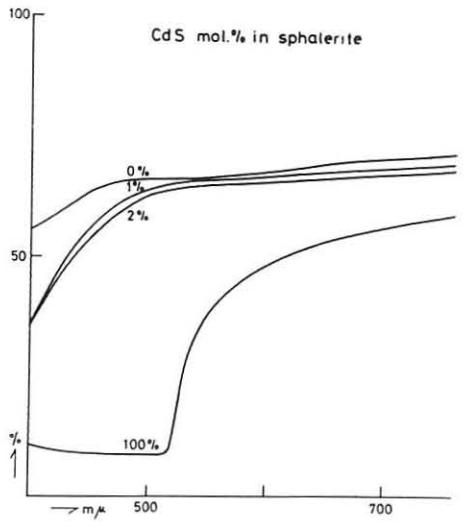


Text-Fig. 2 Trichromatic specification diagram of sphalerite in ZnS-FeS solid solution system. The lightness, whiteness, and saturation in colour are shown in percentage.

Both MnS and CdS are contained in natural sphalerite in amounts less than 2%, and their influence upon the whiteness and trichromatic subordinate properties is clearly indicated as compared with cell dimensions of crystal structure (Skinner 1958, 1959, Kullerud 1953).



Text-Fig. 3 (Left) Spectroscopic reflectivity of sphalerite in which the Mn ion substitutes for Zn ion. Numbers above each curve show MnS mol. % in sphalerite. See Text-fig. 1 for abscissa and ordinate.



Text-Fig. 4 (Right) Spectroscopic reflectivity of sphalerite in which the Cd ion substitutes for Zn ion. Numbers above each curve show CdS mol. % in sphalerite. See Text-Fig. 1 for abscissa and ordinate.

Table 2 Trichromatic coefficients of sphalerite in which the Mn ion substitutes for Zn ion. See Table 1 for the notations.

MnS%	Y (%)	Pe (%)	W (%)	λ (mμ)
0	66.6	32.	66.4	colourless
1	66.0	4.8	65.8	577 (yel.)
3	59.4	5.8	59.1	578 (yel.)
5	52.7	5.2	52.5	573 (gr. yel.)

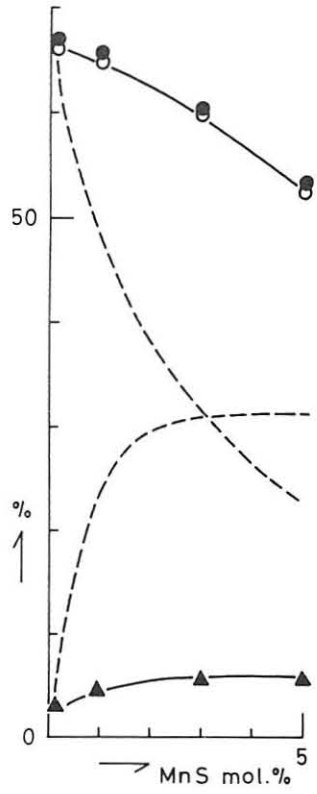
Table 3 Trichromatic coefficients of shalerite in which the Cd ion substitutes for Zn iron. See Table 1 for the notations.

CdS%	Y(%)	Pe (%)	W (%)	λ (mμ)
0	66.6	3.2	66.4	colourless
1	65.7	8.4	65.5	570 (gr. yel.)
2	64.4	9.8	64.1	571 (gr. yel.)
100	38.6	,55.2	17.4	584 (yel. or.)

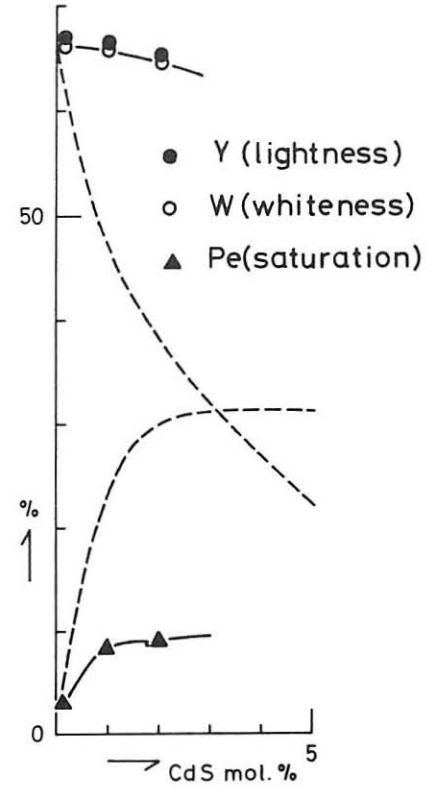
The relation between trichromatic subordinate properties and chemical components in sphalerite is given in Text-Fig. 7, from the above mentioned experimental results. This diagram indicates that the whiteness of sphalerite in which the FeS content substituting for ZnS increases from 0% to 20%, decrease from 72% to 12% straightly. This relation may be used to estimate the iron content in natural sphalerite.

Conclusion

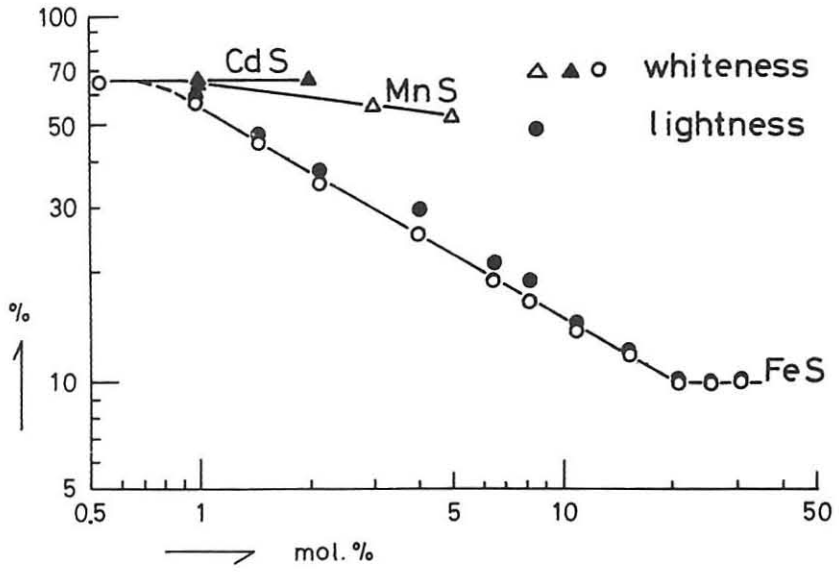
From the systematical experiments on sphalerite of various occurrences and synthetic materials, the writer discussed distinct relations between some chemical components and spectrochromatic properties, with the following conclusion.



Text-Fig. 5 (Left) Trichromatic specification diagram of sphalerite in ZnS-MnS solid solution system.



Text-Fig. 6 (Right) Trichromatic specification diagram of sphalerite in ZnS-CdS solid solution system.



Text-Fig. 7 The relation between trichromatic subordinative properties and chemical components in sphalerite substituting for Zn ion on crystal structure.

The results of the present experiments support the conclusion obtained in the previous papers and also added the new facts: The dominant wave length for hue in colour is almost constant regardless of iron content, but changes slightly toward long wave length according to the increasing Fe content. The influence of FeS content upon the saturation is distinguished under 2% and saturation value amounts to 30% for maximum and whiteness of sphalerite in which the FeS content substituting for ZnS increase from 0% to 15%, decrease from 72% to 12% straightly.

In natural sphalerite, the influence of MnS and CdS upon the whiteness and trichromatic subordinative properties is clear, as compared with cell dimensions.

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