Synthesis of Scheelite Group Minerals in the CaWO_4 - CaMoO_4 - PbMoO_4 - PbWO_4 System from Aqueous Solutions at 100 °C*

by Takako NAKAMURA¹, Kai SUGIYAMA², Emi MORIGUCHI²
and Tetsuya SHOJI³

Scheelite group minerals in the CaWO_4 - CaMoO_4 - PbMoO_4 - PbWO_4 system have been synthesized at 100 °C by mixing of Na_2WO_4 , Na_2MoO_4 , CaCl_2 , and PbCl_2 aqueous solutions. Powder X-ray diffraction data show that complete solid solutions exist in the CaWO_4 - CaMoO_4 and PbWO_4 - PbMoO_4 systems. On the other hand, solid solution are restricted near the end members in the CaWO_4 - PbWO_4 and CaMoO_4 - PbMoO_4 systems. All compounds belonging to the CaWO_4 - CaMoO_4 system show fluorescent colors from cyan to yellow. In contrast, only compounds containing PbMoO_4 mole% from 0.5 to 1 show dark fluorescent color of pale green in the PbWO_4 - PbMoO_4 system.

KEY WORDS : CaWO_4 , CaMoO_4 , PbMoO_4 , PbWO_4 , Fluorescence

1. Introduction

Scheelite (CaWO_4) and powellite (CaMoO_4) are ore minerals of containing tungsten and molybdenum, respectively. Stolizite (PbWO_4) and wulfenite (PbMoO_4) also contain these metals, but they are rare in nature. They have the same structural formula of $A^{2+}B^{6+}O_4$, and belong to the same space group of $C_{4h}^6 - I4_1/a$.

It is well known that among minerals scheelite shows cyan fluorescent color, and that the color changes from cyan to yellow with increasing amount of molybdenum replacing tungsten (e.g. Greenwood, 1943; Kröger, 1948; Vermaas, 1952; Hsu and Galli, 1973). Recently the scintillation property of PbWO_4 has been investigated for applying calorimeter (e.g. Barishevski et al., 1992; Lecoq et al., 1995).

In the CaWO_4 - CaMoO_4 system, a complete solid solution is easily synthesized by a soft processing of mixing of aqueous solutions at room temperature (Shoji and Sasaki, 1978). Strunz (1970) suggests a solid solution series in the PbWO_4 - PbMoO_4 system based on chemical data of natural minerals. Any study has not revealed, however, the relation between the CaWO_4 - CaMoO_4 and PbWO_4 - PbMoO_4 solid solution series.

Based on the above-stated facts the present study has been carried out on the following purposes: 1) to synthesize the minerals in the CaWO_4 - CaMoO_4 (C-WM), PbWO_4 - PbMoO_4 (P-WM), CaWO_4 - PbWO_4 (CP-W) and CaMoO_4 - PbMoO_4 (CP-M) system using a soft processing technique of mixing of aqueous solutions at about 100 °C; 2) to determine the solubility relation in the system; and 3) to reveal the relation between the fluorescent color and the composition of the products.

2. Experiments

2 · 1 Synthesis

In the C-WM system, a CaCl_2 solution and Na_2WO_4 - Na_2MoO_4 mixed solutions whose $Mo/(W+Mo)$ ratios were 0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 were prepared, and mixed at about 100 °C. When a Na_2WO_4 - Na_2MoO_4 solution was dropped into a CaCl_2 solution, a white precipitate appeared immediately. The reaction in this experiment is written as follows:

In this way, the precipitate succeeds to the Mo/W ratio of a mixed solution (Shoji and Sasaki, 1978). In contrast, if a CaCl_2 solution is dropped into the mixed solution, the Mo/W ratio of the precipitate differs from the ratio of the mixed solution, because the ratio of the precipitate is controlled by the distribution coefficient of Mo/W ratio between the solution and the precipitate.

Compounds belonging to the P-WM system were also synthesized by the same method, where a PbCl_2 solution and Na_2WO_4 - Na_2MoO_4 mixed solutions were prepared. The solubility of PbCl_2 at room temperature is low. For this reason, 100 °C was chosen in this work.

In the CP-W system, CaCl_2 - PbCl_2 mixed solutions and a NaWO_4 solution were prepared. The $Pb/(Ca+Pb)$ ratios of mixed solutions were 0, 0.005, 0.01, 0.02, 0.04, 0.06, 0.1, 0.2, 0.4, 0.6, 0.8, 1. Similarly, in the CP-M system, CaCl_2 - PbCl_2 mixed solutions and a Na_2MoO_4 solutions were prepared.

2 · 2 Characterization

All synthesized products were characterized by powder X-ray diffraction (XRD; Rigaku Geiger-flex RAD-IIIB diffractometer), where monochromatic CuK_α was used with an acceleration voltage of 40 kV and a tube current of 20 mA. Spacings were measured accurately at the 004 and 200 peaks in the system of P-WM, and at the 112 peak in the other systems.

* Received July 13, 2001; accepted for publication January 10, 2002

1. Assistant, Department of Environment Systems, School of Frontier Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

2. Department of Geosystem Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

3. Dr. Eng., Professor, Department of Environment Systems, School of Frontier Sciences, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

[For correspondence] FAX 03-3818-7492 (Univ. of Tokyo)

Fig.1 Relation between bulk chemistry and d_{004} and d_{200} values in the PbWO_4 - PbMoO_4 system.

Fig.2 Relation between bulk chemistry and $\Delta 2\theta$ values in the PbWO_4 - PbMoO_4 system.

2 · 3 Fluorescence

All products in the C-WM system, and some products in the P-WM system show fluorescence under short wave ultraviolet ray. Some products in the CP-W system and the CP-M system also show fluorescence, when they are rich in calcium.

In order to simply quantify the fluorescence, all products of the present synthesis were pasted on a black cardboard by agarose (cardboard and agarose are not fluorescent). Two ultraviolet lamps manufactured by S. Hirai were arranged on the slant of the subject. A digital camera (DC260Zoom, Kodak) was also set between the lamps (over the subject). Photos taken by a digital camera were processed by a general-purpose image processing software (Adobe photoshop) and MS-Excel.

3. Results and Discussions

The X-ray diffraction data in the C-WM system agree completely with the data of Shoji and Sasaki (1978).

Fig.1 shows d_{004} and d_{200} values as a function of the bulk chemistry of the starting materials in the P-WM system. The d_{004} value slightly increases with increasing molybdenum content, while the d_{200} value decreases. These trends are clearly observed in the $\Delta 2\theta (=2\theta_{200} - 2\theta_{004})$ value (Fig.2). The gradual change of d-spacings suggests that a continuous solid solution is formed in the P-WM system.

Fig.3 shows X-ray diffraction patterns of the products in

Fig.3 Parts of powder X-ray diffraction patterns of the products in the CaWO_4 - PbWO_4 system.

Fig.4 Relation between bulk chemistry and the d_{112} values in the CaWO_4 - PbWO_4 system.

the CP-W system. Two peaks corresponding to the 112 spacing are recognized in the X-ray diffraction patterns of the products except near the end members. This implies that each product having an intermediate composition consists of two phases. The 112 peaks of the stolzite side slightly shift toward the high angle side, but the peaks of the scheelite side are almost constant. The relation between the bulk chemistry and the d_{112} value in the system is shown in Fig.4. If the d_{112} value of an assumed solid solution series in the CP-W system changes linearly with the composition as shown by a dashed line in Fig.4, the measured d_{112} values indicate that the solid solutions exist near both end members, and that they are immiscible between 0.02 and 0.9 in $\text{Pb}/(\text{Ca}+\text{Pb})$ ratios.

The similar feature appears in the CP-M system (Fig.5). The 112 peaks of the wulfenite side slightly shift toward the high angle side, while the peaks of the powellite side scarcely shift. The relation between the bulk chemistry and the d_{112} value in the system is shown in Fig.6. The solid solution exists

Fig.5 Powder X-ray diffraction patterns of the products in the CaMoO_4 - PbMoO_4 system.

Fig.6 Relation between bulk chemistry and the d_{112} values in the CaMoO_4 - PbMoO_4 system.

in the regions where $\text{Pb}/(\text{Ca}+\text{Pb})$ ratios are lower than 0.05 and higher than 0.8.

The present result suggests the phase relation in the CaWO_4 - CaMoO_4 - PbMoO_4 - PbWO_4 system at 100 °C as shown in Fig.7. A wide immiscibility region (i.e. two phase region) exists between the scheelite-powellite solid solution series and the stolzite-wulfenite one. The solubility of calcium in the stolzite-wulfenite solid solution is higher than that of lead in the scheelite-powellite solid solution.

It is well known that the scheelite-powellite solid solution series shows fluorescence. Some products in the stolzite-wulfenite series show also fluorescence. Shoji and Sasaki (1978) analyzed spectroscopically the fluorescent color in the former series, and showed quantitatively the color change depending on the composition. In the present study, fluorescent color was simply analyzed using a digital camera. Figs.8 and 9 show the relations between fluorescent color intensities and compositions in the scheelite-powellite series, and the stolzite-wulfenite series, respectively. Since they show the change of

Fig.7 A proposed phase diagram in the CaWO_4 - CaMoO_4 - PbWO_4 - PbMoO_4 system at 100 °C.

Fig.8 Relation between $100 \cdot \text{Mo}/(\text{W}+\text{Mo})$ ratio and fluorescent color intensities in the scheelite-powellite series. The intensities were obtained by a digital camera.

Fig.9 Relation between $100 \cdot \text{Mo}/(\text{W}+\text{Mo})$ ratio and fluorescent color intensities in the stolzite-wulfenite series. The fluorescence is recognized at the region, between 0.5–1 PbMoO_4 %mole.

each principal color depending on the composition, it is difficult to understand the change of color tint. As shown in Fig.10, the colors of the scheelite-powellite series are distributed near the basal plane of the HSI (hue-saturation-intensity) color space, and change approximately along the C-W-Y line. In contrast, the color of the stolzite-wulfenite series changes along the K-W axis.

Fig.11 shows the relation between the color saturation and the composition in the scheelite-powellite series, where the saturations are given as -1, 0 and +1 for cyan (C), white (W) and yellow (Y), respectively. According to Fig.11, the saturation changes rapidly from 0 to 0.05 in $\text{Mo}/(\text{W}+\text{Mo})$ ratio, and grad-

Fig. 10 A perspective of the HSI (hue-saturation-intensity) color space where fluorescent colors of Ca(W, Mo)O_4 (open circles) and Pb(W, Mo)O_4 (solid circles) are plotted. Abbreviations: R=red, Y=yellow, G=green, C=cyan, B=blue, M=magenta, W=white and K=black.

Fig. 11 Relation between $100 \cdot \text{Mo}/(\text{W}+\text{Mo})$ ratio and color saturation in the scheelite-powellite series. The vertical axis represents the C-W-Y line in the HSI color space (Fig. 10). The saturation values are -1, 0 and +1 for C, W and Y in the HSI color space, respectively.

usually beyond 0.05. If we use this diagram, the composition of scheelite-powellite series can be estimated within an accuracy of 0.005 where the $\text{Mo}/(\text{W}+\text{Mo})$ ratio is lower than 0.05.

The wulfenite-stolzite series has no fluorescent character in most of the compositional region, but some members show weak fluorescence of pale green. The compositions of the fluorescent members are varied between 0.005 and 0.01 in $\text{Mo}/(\text{W}+\text{Mo})$ ratios. The relation between $\text{Mo}/(\text{W}+\text{Mo})$ ratio and intensity of fluorescent color is shown in Fig. 12, where the vertical axis represents the value (intensity) along the K-W axis in the HSI color space (Fig. 10). The intensity is high at the compositions between 0.005 and 0.01 in $\text{Mo}/(\text{W}+\text{Mo})$ ratios.

The calibration curves shown in Figs. 11 and 12 are not universal, because the saturation and intensity of the fluorescence depend on properties of the ultraviolet lamps, the digital camera, the computer hardware and the processing software used here as well as the chemistry of the solid solution series. However, such kinds of calibration curves can be easily drawn

Fig. 12 Relation between $100 \cdot \text{Mo}/(\text{W}+\text{Mo})$ ratio and color intensity in the stolzite-wulfenite series. The vertical axis corresponds to the K-W line in the HSI color space (Fig. 10).

as stated previously: 1) the solid solution series are easily synthesized by a soft processing; and 2) the fluorescence is easily measured by the combination of conventional tools.

4. Conclusions

Scheelite group minerals in the CaWO_4 - CaMoO_4 - PbMoO_4 - PbWO_4 system were synthesized by mixing of Na_2WO_4 , Na_2MoO_4 , CaCl_2 , and PbCl_2 aqueous solutions at 100°C . The followings are the obtained conclusions.

(1) Complete solid solutions exist in the CaWO_4 - CaMoO_4 and PbWO_4 - PbMoO_4 systems. In contrast, solid solutions are restricted near the end members in the CaWO_4 - PbWO_4 and CaMoO_4 - PbMoO_4 systems.

(2) The Ca(W, Mo)O_4 series shows bright fluorescent from cyan to yellow in all compositional region. On the other hand, the Pb(W, Mo)O_4 series shows dark fluorescence of pale green at only compositions between 0.005 and 0.01 in $\text{Pb}/(\text{Ca}+\text{Pb})$ ratios.

Acknowledgements The authors thank Prof. H. Honma of Tokyo Gakugei University for helpful advices.

References

- Baryshevsky, V. G., Korzhik, M. V., Moroz, V. I., Pavlenko, V. B., Lobko, A. S. and Fyodorov, A. A. (1992): Single crystal of tungsten compounds as promising materials for the total absorption detectors of the e.m. calorimeters, Nucl. Instr. & Meth. A, No. 322, p. 231–234.
- Greenwood, R. (1943): Effect of chemical impurities on scheelite fluorescence, Econ. Geol., Vol. 38, No. 1, p. 56–64.
- Hsu, L. C. and Galli, P. E. (1973): Origin of the scheelite-powellite series of minerals, Econ. Geol., Vol. 68, p. 681–696.
- Kröger, F. A. (1948): Some aspects of the luminescence of solids, New York Elsevier, xi, p. 310.
- Lecoq, P., Dafinei, I., Auffray, E., Schneegans, M., Korzhik, M. V., Missevitch, O. V., Pavlenko, V. B., Fedorov, A. A., Annenkov, A. N., Kostylev, V. L. and Ligon, V. D. (1995): Lead tungstate (PbWO_4) scintillators for LHC EM calorimetry, Nucl. Instr. & Meth. A, No. 365, p. 291–298.
- Shoji, T. and Sasaki, N. (1978): Fluorescent color and X-ray powder data of synthesized scheelite-powellite series as guides to determine its composition, Mining Geology, Vol. 28, p. 397–404.
- Strunz, H. (1970): Mineralogische Tabellen, 5. Auflage, p. 301–302.
- Vermaas, F. H. S. (1952): South african scheelites and an X-Ray method for determining members of the scheelite-powellite series, Amer. Mineral., Vol. 37, p. 719–735.

(和文要旨: 次頁につづく)

CaWO_4 - CaMoO_4 - PbMoO_4 - PbWO_4 系固溶体の 100 °C, 常圧下における合成

中 村 貴 子¹ 杉 山 快² 森 口 恵 美³ 正 路 徹 也⁴

100 °C, 常圧下において, Na_2WO_4 , Na_2MoO_4 , CaCl_2 , PbCl_2 の混合水溶液から CaWO_4 - CaMoO_4 - PbMoO_4 - PbWO_4 系鉱物を合成した。粉末 X 線回折の結果によると, CaWO_4 - CaMoO_4 系と PbMoO_4 - PbWO_4 系の合成物は完全固溶体を形成している。一方, CaWO_4 - PbWO_4 系と CaMoO_4 - PbMoO_4 系では固溶体はそれぞれ端成分付近に限られている。 CaWO_4 - CaMoO_4 系合成物は短波長の紫外線を照

射すると, 淡青色から黄色の明るい蛍光色を示す。一方, PbMoO_4 - PbWO_4 系固溶体では, PbMoO_4 分子を 0.5 ~ 1 mole% 含む合成物のみが淡緑色の暗い蛍光を示す。

- 1. 普通会员 東京大学大学院助手 新領域創成科学研究科環境学専攻
 - 2. 東京大学大学院生 工学系研究科地球システム工学専攻
 - 3. 東京大学技術官 工学系研究科地球システム工学専攻
 - 4. 普通会员 工博 東京大学大学院教授 新領域創成科学研究科環境学専攻
- キーワード: 灰重石, パウエル石, モリブデン鉛鉱, 鉛重石, 蛍光