

Preparation Conditions of $\text{LiCeMo}_2\text{O}_8$ as Yellow Pigment by Wet Chemical Synthesis

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(2006年11月30日受理)

In order to substitute the conventional yellow inorganic pigments containing cadmium, lead or Cr(VI), which are toxic and environmentally harmful, we focused on $\text{LiCeMo}_2\text{O}_8$. As Ce^{3+} ion is the origin of the color, the crystalline field around Ce^{3+} ion may be important. Therefore, we have studied the influence of solution compositions and preparation conditions of the compound by wet chemical synthesis. The solution compositions were Li:K=1:0, 40:1, 10:1 and 0:1, the preparation conditions were atmosphere, temperature and time. Crystal parameters of the products were measured by using XRD. The optical parameters were evaluated with the reflectance spectra data of visible wave length 380-700nm.

We found that the optimal conditions are as follows; the alkali metal ion is Li ion, the burning atmosphere is nitrogen, the burning temperature is 600°C, the burning time is 1 hr.

Key word : Inorganic pigment, Cerium, Crystalline field splitting, Wet chemical synthesis, Optical property

1. Introduction

Inorganic pigments are generally superior to organic pigments with regard to light and weather resistance and cheap cost¹⁾. Conventional yellow inorganic pigments are lead chromate, zinc chromate, cadmium sulfide, barium chromate, etc. These chroma are high in spite of inorganic pigments. But these pigments contain harmful elements such as Cr(VI), Pb or Cd.

Recently, environmental problems have been focused. For example, RoHS order was already enforced on Jul. 1st 2006 in Europe. It limits the use of lead, mercury, cadmium, Cr(VI), polybrominated biphenyls, Polybrominated diphenyl ethers. A development of a novel yellow inorganic pigment without harmful elements is requested, because the provision for environment will be emphasized more in future.

Some substances have been proposed. For example, $\text{LiCeMo}_2\text{O}_8$ by wet chemical synthesis

and solid state reaction method^{2,3)}, bismuth vanadate⁴⁾, a pigment based on cerium phosphate⁵⁾, La_2S_3 ⁶⁾ and others. None of these can be equal to the conventional inorganic pigments in vivid yellow and orange color.

In this study, we focus on $\text{LiCeMo}_2\text{O}_8$ as an inorganic pigment containing Ce^{3+} ion. The origin of the color is a 4f-5d transition of Ce^{3+} ion with the absorption of visible light. The absorption coefficient of the transition is large because it is the allowed transition. We aimed the improvement of the hue through the control of the crystalline field splitting of 5d orbital of Ce^{3+} ion.

We have studied the effect of some preparation conditions because they may change lattice parameters of the compound. The examined conditions are solution composition, temperature, atmosphere and time in the drying and burning processes. The strategy of our study is to change the color properties by changing of crystalline field splitting of Ce^{3+} ion.

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2. Experimental

2.1 Sample preparation

Reagents were $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (nacalai tesque), $\text{LiOH} \cdot \text{H}_2\text{O}$ (nacalai tesque, 99%), KOH (nacalai tesque, 85%) and MoO_3 (Wako, 99%). $\text{LiCeMo}_2\text{O}_8$ was prepared by the wet chemical method. A 30 ml of 0.5M- CeCl_3 and AOH (A=Li, K:0.5M-Li, 0.1, 0.4 and 0.5M-K) and 120ml of AOH (A=Li, K:1.0M-Li, 1.5M-K) containing 0.5M- MoO_3 were added into a separable flask. The mixed aqueous solution was stirred at 30°C, 200-250rpm for 24hr to form suspension of the precursor. The suspension was filtrated and dried (in vacuum at room temperature or in atmospheric pressure at 110°C) in a drying chamber. Then the precursor was burned at 400, 500, 600 or 700°C for 1, 3 or 6 hr, in the air or nitrogen in the electric furnace (ADVANTEC, KM-280) or (DENKEN, KDF-75).

2.2 Characterization

The crystalline structure of the powder products was analyzed by powder X-ray diffraction (XRD) (MACSCIENCE, MXP3, target:Cu). Lattice parameters were calculated by using Cell Parameters Calculation Program (CellCalc)⁷⁾.

The reflectance spectra was measured by spectrophotometer (KONICA MINOLTA, CM-3600d) in the range of 380-700nm with D_{65} light source and 10-degree field of view. We evaluated the optical characteristics as excitation purity (P_e) and CIE 1976 $L^*a^*b^*$ system. It is useful to explain reddish-yellow vague hue.

3. Results and Discussion

3.1 Influence of burning temperature and time

We determined the following standard synthesis conditions: the alkali metal ion was Li, the drying condition was the atmospheric pressure at 110°C, the burning atmosphere was the air, the burning time was 6 hr, the burning temperature was 600°C.

XRD patterns and the reflectance spectra of the $\text{LiCeMo}_2\text{O}_8$ at burning temperatures of 400, 500, 600 and 700°C are shown in Fig. 1 and 2,

respectively.

XRD data of $\text{LiCeMo}_2\text{O}_8$ have not been recorded in PDF cards. However, the product was identified as $\text{LiCeMo}_2\text{O}_8$, which had the same diffraction pattern of $\text{LiLa}(\text{MoO}_4)_2$ (PDF card No.18-734) of the tetragonal scheelite structure ($I4_1/a$).

We see from Fig. 1 that crystallinity of sample (b), (c) and (d) became better, because

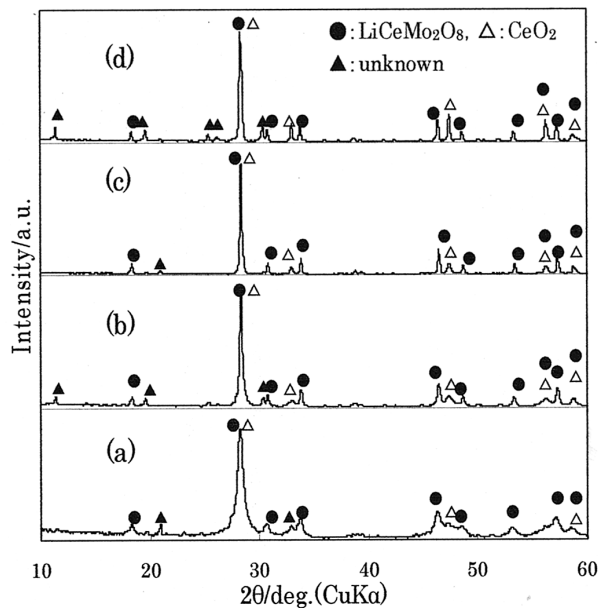


Fig. 1 XRD patterns of the products burned at (a) 400, (b) 500, (c) 600 and (d) 700°C

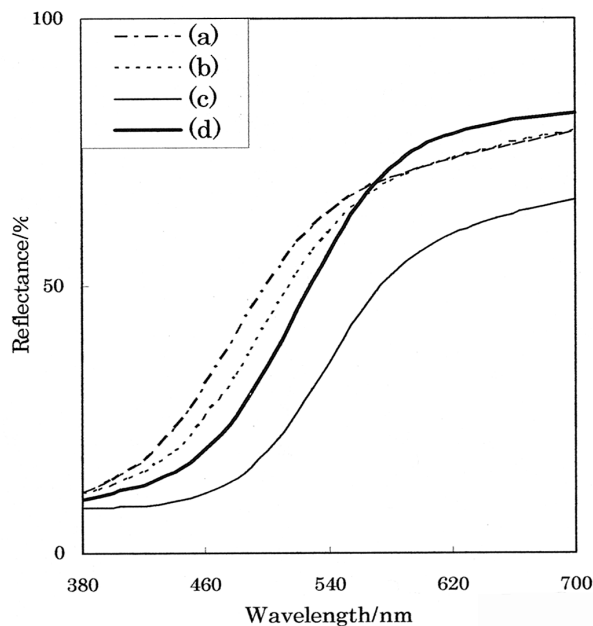


Fig. 2 Reflectance spectra of the products burned at (a) 400, (b) 500, (c) 600 and (d) 700°C

the peak-width became narrower with increasing burning temperature. However, at 700°C , XRD peaks of unknown compound appeared and the intensity of CeO_2 became large. The unknown compound can be Li_2MoO_4 from the solution composition.

We see from Fig. 2 that the difference of the burning temperature influenced the reflectance spectra greatly. Optical parameters L^* , a^* , b^* and excitation purity of the sample from the reflectance spectra data in Fig. 2 are summarized in Table 1. L^* relates to brightness. A positive a^* value indicates redness and a negative a^* value indicates greenness. A positive b^* value indicates yellowness and a negative b^* value indicates blueness. The excitation purity (P_e) is a measure of vividness in human sight.

Table 1 Optical parameters of the products burned at 400-700°C

Burning temperature/°C	L^*	a^*	b^*	$P_e/\%$
(a) 400	83.26	-1.23	38.45	42.22
(b) 500	81.65	2.02	43.88	48.96
(c) 600	68.92	14.87	49.80	63.25
(d) 700	80.69	8.19	51.79	57.99

The color of the sample (c) burned at 600°C was reddish-yellow, sample (b) and (d) were yellow, and sample (a) looked dull yellow.

The excitation purity increased with increasing burning temperature from 400 to 600°C . However, it decreased in sample (d). We suppose that the formation of CeO_2 caused to lower the P_e in the case of sample (d). The burning at 600°C may be optimal. Hence burning temperature was fixed to 600°C in all the rest experiments.

A precipitate dried in vacuum, room temperature was burned for 1, 3 and 6 hr at 600°C .

Both of the optical and lattice parameters did not change with the burning time. It is clear that 1hr is enough for the burning time of the precursor.

3.2 Influence of solution composition

We used Li and K ion as the alkali metal ion. Na ion was not used because of its similar ionic radius to Li. The preparation conditions of the aqueous solutions are shown in Table 2.

XRD patterns and reflectance spectra of the products are shown in Fig. 3 and 4, respectively. The optical and calculated lattice parameters are summarized in Table 3 and 4, respectively.

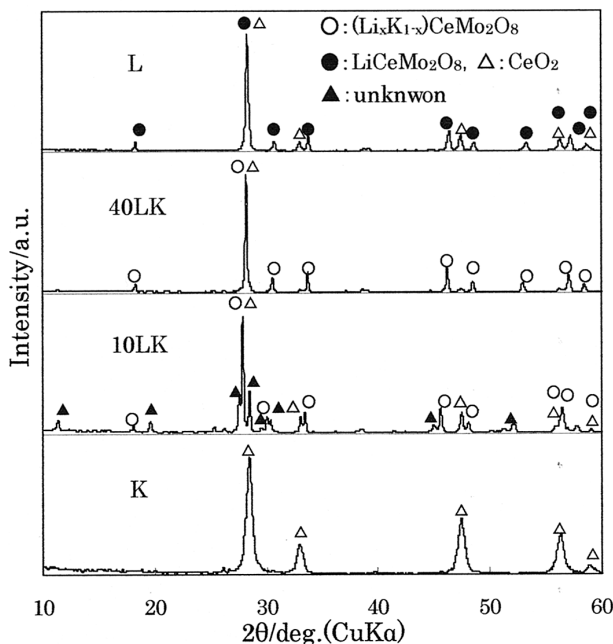


Fig. 3 XRD patterns of L, 40LK, 10LK and K prepared in Li:K=1:0, 40:1, 10:1 and 0:1, respectively

We name the products prepared in Li:K=1:0, 40:1, 10:1 and 0:1, as L, 40LK, 10LK and K, respectively.

We see from Fig. 3 that $\text{LiCeMo}_2\text{O}_8$ and CeO_2 formed in L. However, expected KCeMo_2O_8 was

Table 2 The preparation conditions of the aqueous solutions

	Li : K	0.5M-CeCl ₃ /ml	AOH/ml	AOH containing 0.5M-MoO ₃ /ml
L	1:0	30	30 (0.5M, A=Li)	120 (1.0M, A=Li)
40LK	40:1	30	30 (0.1M, A=K)	120 (1.0M, A=Li)
10LK	10:1	30	30 (0.4M, A=K)	120 (1.0M, A=Li)
K	0:1	30	30 (0.5M, A=K)	120 (1.5M, A=K)

Table 3 Optical parameters of the products obtained by the solution compositions

	Li:K	L^*	a^*	b^*	$P_c/\%$
L	1:0	83.52	3.24	44.72	49.15
40LK	40:1	81.55	3.77	48.45	53.79
10LK	10:1	85.32	-2.20	37.71	40.55
K	0:1	90.77	-4.03	22.87	23.13

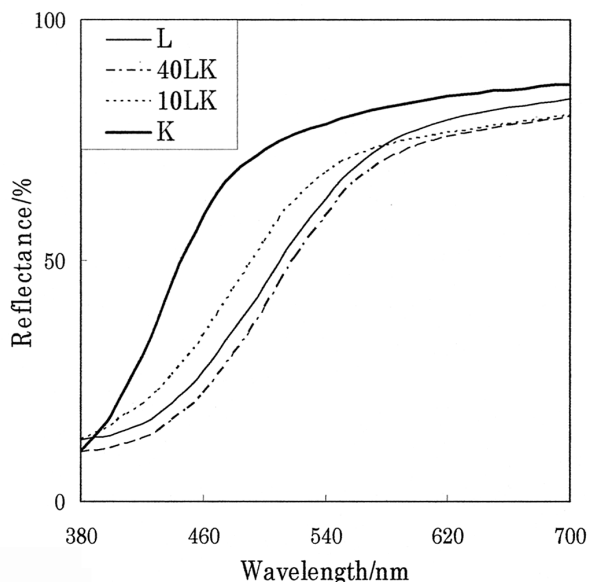


Fig. 4 Reflectance spectra of L, 40LK, 10LK and K prepared in Li:K=1:0, 40:1, 10:1 and 0:1, respectively

Table 4 Lattice parameters of the products obtained by the solution compositions

	Li:K	a/nm	c/nm
L	1:0	0.529	1.15
40LK	40:1	0.530	1.16
10LK	10:1	0.539	1.17

not formed and only CeO_2 was observed in K, and XRD pattern of 10LK was shifted to lower angle than L.

As ionic radius of K ion, 0.151nm with coordination number 8, is much larger than that of Li ion (0.092nm), a scheelite type compound may not precipitate from K solution, while Ce^{3+} ion was oxidized to precipitate CeO_2 .

We also see from Fig. 3 that XRD patterns of the scheelite structure and CeO_2 appear in 10LK and the produced amount of CeO_2 in 10LK is equal to L from the same relative peak intensity. We see from Table 4 that the ratio of the lattice

parameters a and c in 10LK and L, are approximately 1.02. We supposed that the distance between the each of Ce^{3+} ion and O^{2-} ions became 1.02 times.

To obtain the product having high excitation purity, we must sharpen the edge of absorption spectrum.

We see from Fig. 4 that the reflectance spectrum of 10LK was shifted to lower wavelength compared to L. The color of the products shifted to greenish yellow in 10LK. We can confirm the color change from Table 3 that the value of b^* changed from 3.24 to -2.20.

Let us discuss this cause from the point of view of the crystalline field splitting; CFS. A schematic representation of the tetragonal scheelite structure⁹⁾ is shown in Fig. 5.

We see from Fig. 5 that each of Ce^{3+} ion in the scheelite structure is octacoordinated by O^{2-} ions.

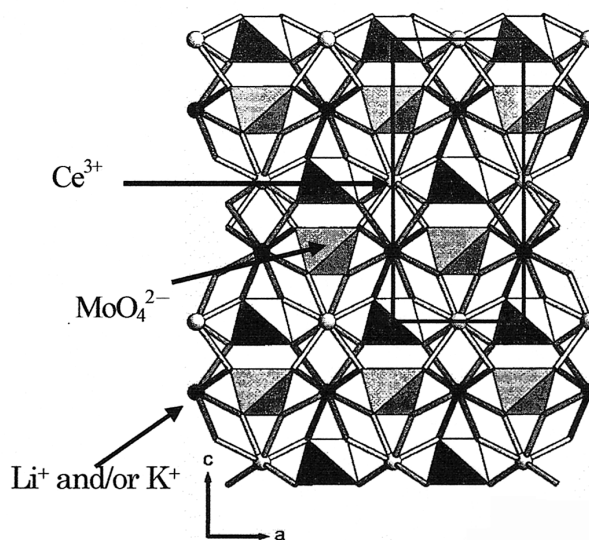


Fig. 5 Schematic representation of the scheelite structure⁹⁾

Electron configuration of ground state of

Ce³⁺ ion is [Xe]4f¹5d⁰. If the Ce³⁺ ion is free ion, 5d-orbitals are degenerate five-fold. We think that the octacoordinated CFS is similar to the tetraordinated CFS. Then, schematic representations of the CFS of L and 10LK in the crystal structures are qualitatively shown in Fig. 6. We ignore the splitting of 4f-orbitals because it would be small.

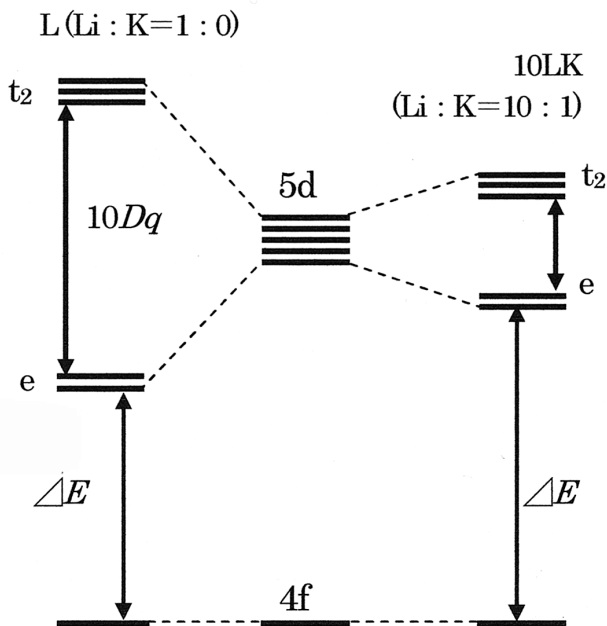


Fig. 6 Schematic representation of the CFS as preparing 1:0 and 10:1 in Li:K ratio

The magnitude of CFS of d-orbitals can be represented $10Dq$. D is a parameter having the information of anions coordinated around the central ion. q is a parameter having the information of the electron taking the interaction in electric field. The D is represented in the following equation¹⁰⁾,

$$D = \frac{35Ze}{4r^5}$$

where, r is the distance between cation and anion, The q is not dependent on r . Ze is absolute value of the charge of anions coordinated around the central ion. From the equation, D is the value that inversely proportionates to the minus fifth power of r .

We supposed that the distance of 10LK between the each of Ce³⁺ ion and O²⁻ ions became

1.02 times of L. Thus, the magnitude of CFS decreased about 10%, if the q is assumed to keep constant.

The absorption of visible light by 4f-5d transition of Ce³⁺ ion is the origin of yellow color of LiCeMo₂O₈. Thus, the absorbing energy of (Li_xK_{1-x})CeMo₂O₈ containing K ions became larger than that of LiCeMo₂O₈. (Li_xK_{1-x})CeMo₂O₈ can not absorb the light of the wavelength that absorbed by LiCeMo₂O₈, reflected. For this reason, the reflectance spectrum of 10LK was shifted to lower wavelength.

3.3 Influence of drying condition and burning atmosphere

We think that causes of generation CeO₂ are in drying and burning steps. Two drying conditions were compared; in vacuum at room temperature (v), in atmospheric pressure at 110 °C (a). However, both generation amounts of CeO₂ did not differ.

We examined the burning atmosphere for the cause of influence of CeO₂ forming. We adopted the alkali metal ions ratio of 10LK.

XRD patterns and the reflectance spectra of the products burned in the air (A) and in nitrogen (N) are shown in Fig. 7 and 8, respectively.

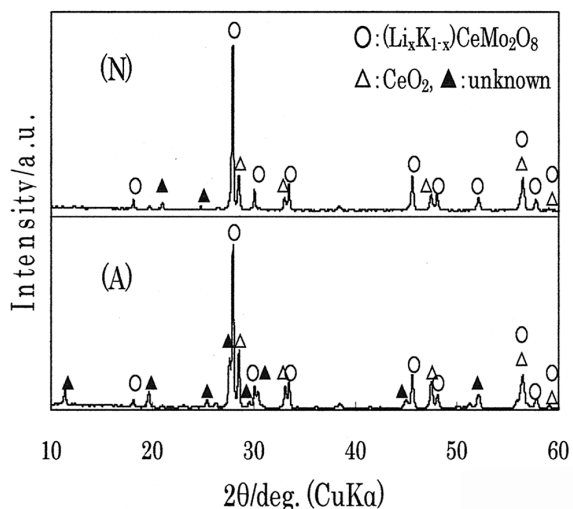


Fig. 7 XRD patterns of the products burned in the air (A) and the nitrogen (N)

Fig. 7 shows that the product (A) contains around 1.8 times more CeO₂ than (N). This is

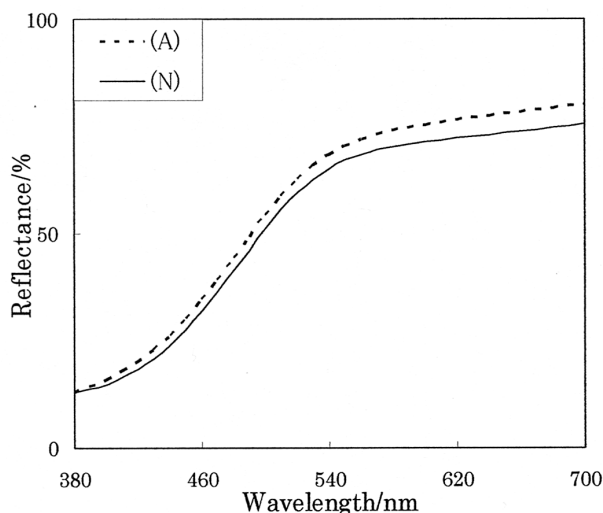


Fig. 8 Reflectance spectra of the products burned in the air (A) and the nitrogen (N)

the reason why L^* of (A); 85.32 is higher than the other of (N); 83.51. Fig. 8 shows that reflectance of (A) is around 6% higher than that of (N) through 400-700nm. This may be caused by white CeO_2 .

4. Conclusions

We examined qualitatively various preparation conditions that could influence on the crystal structures and the optical properties of $\text{LiCeMo}_2\text{O}_8$, and obtained the following conclusions.

- 1) Li ion as the composition of the alkali metal ion component is the best for the $\text{LiCeMo}_2\text{O}_8$ as yellow pigment by wet chemical method.
- 2) For prevention of the formation of CeO_2 that decreases excitation purity, the optimum preparation conditions are as follows; the burning atmosphere is the nitrogen, the burning temperature is 600°C , the burning time is 1 hr.

Acknowledgement

We would like to thank Mr. Yamaguchi and Mr. Tsukamoto of Dainichiseika Color & Chemicals Mfg. Co., Ltd. for measurements of the reflectance spectra.

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