Colour possibilities of the $CuAl_{2-x}Ln_xO_4$ pigments

Žaneta Dohnalová, Petra Šulcová, Miroslav Trojan

Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Czech Republic
e-mail: zaneta.dohnalova@upce.cz

Abstract

Our attention was focused on preparation of mixed metal oxide pigments doped with ions of lanthanides with the general formula $CuAl_{2-x}Ln_xO_4$, where x = 0 to 2 and Ln = Eu, Sm, Nd, Y, La, Tm. The pigments were synthesized by solid state reactions at high calcination temperatures of 900-1100°C. The resultant colour impression of the pigments was related to ionic radii of rare earth cations. Trivalent rare earth ions with ionic radii bigger than 0.092 nm (Sm, Nd, Eu and La) caused the formation of black color pigments, whereas the formation of turquoise pigments was conditioned by size of ionic radii less than 0.092 nm (Y, Tm).

Temperature 900°C was not suitable for the synthesis of this kind of pigments. On the diffraction pattern of the $CuAl_2O_4$ sample, unreacted CuO was identified next to the spinel compound. Besides, the higher calcination temperatures (1000 and 1100°C) caused the formation of darker black and deeper turquoise pigments.

Keywords: Pigments, colour, solid state reaction, spinels, perovskite

MOŻLIWOŚCI BARWNE PIGMENTÓW $CuAl_{2-x}Ln_xO_4$

Naszą uwagę skupiliśmy na preparatyce pigmentów z mieszanych tlenków metali, dotowanych jonami lantanowców. Ogólny wzór tych pigmentów był: $CuAl_{2-x}Ln_xO_4$, gdzie x zawarty był w granicach 0-2, a za Ln podstawiano: Eu, Sm, Nd, Y, La, Tm.

Syntezę pigmentów prowadzono w drodze reakcji w fazie stałej, w zakresie temperatur 900-1100°C. Barwa pigmentów związana była z promieniem jonowym kationów ziem rzadkich. Jony trójwartościowe, o promieniu jonowym większym od 0,0092 nm (Sm, Nd, Eu i La) powodowały powstawanie pigmentów o barwie czarnej, podczas gdy powstawanie pigmentów turkusowych było uwarunkowane promieniem jonowym mniejszym od 0,092 nm (Y, Tm).

Temperatura syntezy 900°C była za niska do syntezy w/w pigmentów, ponieważ dyfraktogramy próbek syntezowanych w tej temperaturze, obok $CuAl_2O_4$, wykazały obecność nieprzereagowanego CuO. W wyższych temperaturach kalcynacji (1000 i 1100°C) powstawały pigmenty o głębszej barwie, zarówno czarnej jak i turkusowej.

Słowa kluczowe: pigmenty, barwa, reakcje w stanie stałym, spinele, perowskity

Introduction

Compound $CuAl_2O_4$ belongs to the group of spinel pigments of the first type with cubic structural arrangement of oxygenic anions. According to a way of occupying the interstices, the compound is classified to the group of normal spinels. The Cu^{2+} ions occupy 1/8 of the tetrahedral interstices and Al^{3+} ions occupy 1/2 of the octahedral interstices [1]. As already described, the (100) surface slab with Cu^{2+} ions is created with $b = c = 0.8064$ nm, where two formula units of $CuAl_2O_4$ are contained (Fig. 1a). The (100) surface is fully optimized where the calculated b and c are 0.7694 nm and 0.7687 nm, respectively. The equilibrium bond length of Cu–O is 0.178 nm, and the corresponding O–Cu–O bond angle is 126.1 ° as shown in Fig. 1b [2].

Aluminum hydroxide and cupric nitrate are the most often used reactants for the synthesis of $CuAl_2O_4$. The recommended calcination temperature is 1000-1100°C [3, 4].

$CuLn_2O_4$ compounds belong to the group of mixed metal oxides pigments. These pigments can be considered as a subcategory of complex inorganic coloured pigments. The term mixed metal oxide, does not the represent reality as these pigments are not the mixtures, but solid solutions or compounds consisting of two or more metal oxides. Each pigment has a defined crystal structure which is determined by the host lattice. Other oxides interdiffuse at the high temperature into the host lattice structure by forming either a solid-state solution or a new compound [5]. The crystal structure of a series of $CuLn_2O_4$ is termed as the layered-perovskite structure, where the characteristic two-dimensional CuO_2 sheets and other sheets are stacked along the c axis [6,7]. The $CuLn_2O_4$ compounds with orthorhombic crystal lattice [8] can be prepared by the solid state reaction at high temperatures. Watanabe et. all described the phase composition of a mixture containing La_2O_3 and CuO and calcined at the temperature range of 1000-1300°C [9]. From the pigment application point of view, the compounds of general formula $Ln_2O_3{\cdot}2CuO$, where Ln = Tb, Lu, Y, Sc, have been investigated [10]. The green coloured pigments were synthesised by the solid state reaction at the temperature range of 950-1050°C. The pigments are two phase systems containing next to the main $Ln_2O_3{\cdot}2CuO$ product also unreacted CuO. The pigments are resistant to the effect of ceramic glaze.

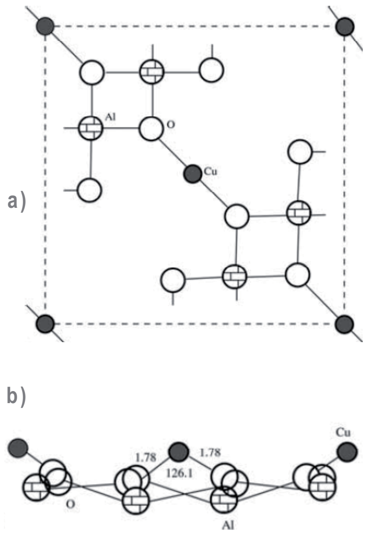

Fig. 1. a) Top view of the $CuAl_2O_4$ (100) surface, b) side view of the fully relaxed $CuAl_2O_4$ (100) surface [2]

Our attention was focused on the preparation of mixed metal oxide pigments of composition $CuAl_2O_4$, $CuAlLnO_4$, $CuAl_{1.5}Ln_{0.5}O_4$, $CuAl_{0.5}Ln_{1.5}O_4$ and $CuLn_2O_4$ where Ln = Eu, Sm, Nd, Y, La, Tm. The quality of pigments is described by their colour properties, particle size distribution and phase composition.

Experimental

The reagents such as CuO (Heubach,GmbH, SRN), Ln_2O_3 (Indian Rare Earths Ltd., India) and $Al(OH)_3$ (BDH., GB) were weighed in suitable molar proportions and subsequently ground manually in a porcelain mortar to obtain a homogenous reaction mixture. The reaction mixtures were heated at the temperature range of 900–1100°C (step 100°C) for 3 hours in an electric resistance furnace. The heating rate was 5°C/min. Corundum crucibles were used. The samples were gradually cooled to room temperature and ground in an agate mortar.

The samples of pigments were formulated into an organic matrix in a mass tone format and evaluated with respect to their colour properties by measuring of the spectral reflectance. The measurement was carried out in the visible region of light (ColourQuest XE (HunterLab, USA)). The measuring system used the CIE L*a*b* colour. Here, the coordinate L* expresses degree of brightness and the coordinates a* and b* describe the colour hue. Thorough description of colour is done by recalculation of chroma extent C, according to the formula $C = (a^{*2}+b^{*2})^{1/2}$. The next measurement conditions involved: illuminant D65 (6500 K), 10° complementary observer, the geometry of measurements being d/8°.

The particle size distribution of the samples was measured by using a Mastersizer 2000/MU (Malvern Instruments, UK). The equipment employs the scattering of incident light on particles. The solids were ultrasonically homogenized for 90 seconds and measured in a solution with $Na_4P_2O_7$ (c = 0.15 mol/dm^3). The signal was evaluated on the basis of Fraunhofer bending.

The crystal structures of the powdered materials were studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using a Brucker (GB) difractometer D8 (Bruker, GB) with a goniometer of 17 cm in the 2Θ range of 10-80°. The Cu $K_{\alpha1}$ (λ = 0.15418 nm) radiation was used for the angular range of 2Θ < 35° and Cu $K_{\alpha2}$ (λ = 0.15405 nm) for the range of 2Θ > 35. A scintillation detector was used.

Results

The colour properties of all samples prepared by calcination at 1000°C are summarised in Table 1. The pigments of general formula $CuAl_{2-x}Ln_xO_4$, where x = 0, 0.5, 1, 1.5, 2 and Ln = Eu, Sm, Nd, Y, La, Tm can not be described by one colour. Spinel compound $CuAl_2O_4$ was the primary prepared pigment. This pigment provided deep brown colour hue. Increasing amount of Ln^{3+} to Al^{3+} substitution (where Ln = Eu, Sm, Nd and La) leaded to the change of colour hue from deep brown ($CuAl_2O_4$) through dark brown ($CuAl_{1.5}Ln_{0.5}O_4$, $CuAl_{1.5}Ln_{0.5}O_4$, $CuAlLnO_4$) to black colour ($CuLn_2O_4$). The values of all colour coordinates have decreasing character with increasing amount of lanthanide ions in the pigments at all calcination temperatures (900-1100 °C). The *a**, *b** colour co-ordinates describing the colour hue shifted closer to the center of Hunter`s colour diagram and this indicates the formation of pigments with very dark black colour. Also very low values of lightness (*L**) and chroma (*C*) signalise the black colour of a good quality. The darkest and therefore the best black colour can be prepared by total Al^{3+} substitution by the europium cations. The pigments that contained yttrium cation and thulium cation changed their colour properties from deep brown through dark green ($CuAl_{1.5}Ln_{0.5}O_4$, $CuAl_{1.5}Ln_{0.5}O_4$, $CuAlLnO_4$) to the intensive turquoise colour hue ($CuLn_2O_4$). The pigments with rising amount of lanthanide cations (x = 0.5, 1) had darker and

Tab. 1. Colour properties of the samples $CuAl_{2-x}Ln_xO_4$ (calcination temperature of 1000°C)

Sample	L*	a*	b*	C
$CuAl_2O_4$	40.32	16.64	16.00	23.08
$CuAl_{1.5}Eu_{0.5}O_4$	33.51	5.74	5.20	7.75
$CuAl_{1.5}Sm_{0.5}O_4$	33.59	6.12	5.80	8.43
$CuAl_{1.5}Nd_{0.5}O_4$	36.95	6.42	5.84	8.68
$CuAl_{1.5}Y_{0.5}O_4$	37.36	6.30	7.55	9.83
$CuAl_{1.5}La_{0.5}O_4$	36.48	5.78	5.26	7.82
$CuAl_{1.5}Tm_{0.5}O_4$	38.39	4.52	7.91	9.11
$CuAlEuO_4$	28.94	2.08	1.38	2.50
$CuAlSmO_4$	29.32	2.20	1.29	2.55
$CuAlNdO_4$	30.04	1.87	0.58	1.96
$CuAlYO_4$	35.64	-4.19	1.23	4.37
$CuAlLaO_4$	29.52	2.08	0.58	2.16
$CuAlTmO_4$	37.64	-5.76	1.65	5.99
$CuAl_{0.5}Eu_{1.5}O_4$	26.32	1.38	0.50	1.47
$CuAl_{0.5}Sm_{1.5}O_4$	27.97	1.17	-0.11	1.18
$CuAl_{0.5}Nd_{1.5}O_4$	27.05	0.97	-0.68	1.18
$CuAl_{0.5}Y_{1.5}O_4$	37.58	-11.76	-2.74	12.07
$CuAl_{0.5}La_{1.5}O_4$	27.70	0.93	-0.62	1.12
$CuAl_{0.5}Tm_{1.5}O_4$	39.45	-13.60	-1.20	13.65
$CuEu_2O_4$	25.89	0.73	-0.52	0.90
$CuSm_2O_4$	25.85	0.74	-0.68	1.00
$CuNd_2O_4$	24.28	0.78	-0.73	1.07
CuY_2O_4	39.24	-21.75	-6.81	22.79
$CuLa_2O_4$	26.67	0.81	-0.67	1.05
$CuTm_2O_4$	41.61	-23.07	-4.20	23.45

less rich colour hue than the primary pigment (x=0). The values of lightness and chroma again increased with increasing amount of the lanthanide cations. The $CuYl_2O_4$ pigment has more interesting turquoise hue than the $CuTm_2O_4$ pigment. Minor amount of green hue (-*a**) and at the same time major amount of blue hue (-*b**) contribute to the formation of more interesting turquoise colour of the $CuYl_2O_4$ pigment.

Tab. 2. Colour properties of the samples $CuAl_{2-x}Ln_xO_4$ (heating temperature of 1000°C)

Sample	T [°C]	L*	a*	b*	C
$CuAl_2O_4$	900	36.45	14.20	11.59	18.33
$CuAl_2O_4$	1000	40.32	16.64	16.00	23.08
$CuAl_2O_4$	1100	37.23	14.90	16.73	24.61
CuY_2O_4	900	41.30	-21.04	-6.11	21.91
CuY_2O_4	1000	39.24	-21.75	-6.81	22.79
CuY_2O_4	1100	38.66	-22.52	-6.51	23.44
$CuEu_2O_4$	900	26.06	0.73	-0.81	1.09
$CuEu_2O_4$	1000	25.89	0.73	-0.52	0.90
$CuEu_2O_4$	1100	22.56	0.88	-0.03	0.88

Calcination temperature had significant effect on the colour properties of all samples. The effect of calcination temperature on the colour properties of the brown pigment ($CuAl_2O_4$), the turquoise pigment (CuY_2O_4) and the black pigment ($CuEu_2O_4$) shows Table 2. Synthesis of the good quality brown pigment ($CuAl_2O_4$) was conditioned by the calcination temperature of 1000°C, which is necessary for creation of rich colour hue and the highest value of co-ordinate *a** - reflecting amount of red hue. Interesting colour hue of the $CuAl_2O_4$ pigment connects with its phase composition. Unreacted cupric oxide was identified at the X-ray diffraction pattern of the sample $CuAl_2O_4$ heated at 900°C. Single phase pigment with the cubic crystal structure can be prepared by heating at 1000°C and more. A lattice parameter of the cubic structure was 0.8075 nm (Fig. 2).

Lightnes of the turquoise pigments slightly decreased with the rising calcining temperature. Values expressing colour hue are almost stable at all calcining temperatures and the chroma of the pigments increased with the temperature (Tab. 2). The pigments contain unreacted yttrium oxide at all calcination temperatures (Fig. 3). From the pigmentary application point of view, the calcination temperature 1000°C is an adequate temperature for the synthesis of two phase turquoise inorganic pigment of a good quality.

It is appropriate to synthesize the black inorganic $CuEu_2O_4$ pigment by solid state reaction at 1100°C. The temperature growth from 900°C to 1100°C causes the darkening of the pigment and shifted the values of *a** and *b** to the center of a colour cross. Chroma of the pigment was low.

All pigments were characterised by measuring the particle size distribution. The values of median (d_{50}) vary in the range of 4-14 μm and do not refer any specific trend depending on the change of composition of the pigments. Comparison of the distribution width showed wider particle size distributions of the pigments that contained the lanthanide cations. The particle size distribution of the powdered $CuAl_{2-x}Y_xO_4$ pigments is shown in Table 3.

Tab. 3. Particle size distribution data for powder $CuAl_{2-x}Y_xO_4$ pigments

Sample	d_{10} [μm]	d_{50} [μm]	d_{90} [μm]
$CuAl_2O_4$	2.33	10.87	24.72
$CuAl_{1.5}Y_{0.5}O_4$	3.61	13.19	27.24
$CuAlYO_4$	2.75	9.66	24.57
$CuAl_{0.5}Y_{1.5}O_4$	1.48	6.56	29.59
$CuYl_2O_4$	1.99	10.58	63.43

Conclusions

The main attention was focused on a study of pigmentary application properties of mixed metal oxide pigments containing the lanthanide cations. The general formula $CuAl_{2-x}Ln_xO_4$, where x = 0, 0.5, 1.0, 1.5 and 2 and Ln = Eu, Sm, Nd, Y, La, Tm fully describes composition of the synthesized pigments. The pigments were synthesized by solid state reaction conducted at 900-1100°C. The resultant colour impression of the pigments was related to ionic radii of the rare earth cations. Trivalent rare earth ions with ionic radii bigger than 0.092 nm (Sm, Nd, Eu and La) caused the shift of colour co-ordinates *a**, *b** close to 0 and the formation of black color pigments ($CuLn_2O_4$). The ytrium and thulium cations, having size of ionic radii less than 0.092 nm, shifted the resultant colour to the field of green hue and the CuY_2O_4 and $CuTm_2O_4$ pigments provided the rich turquoise colour hue.

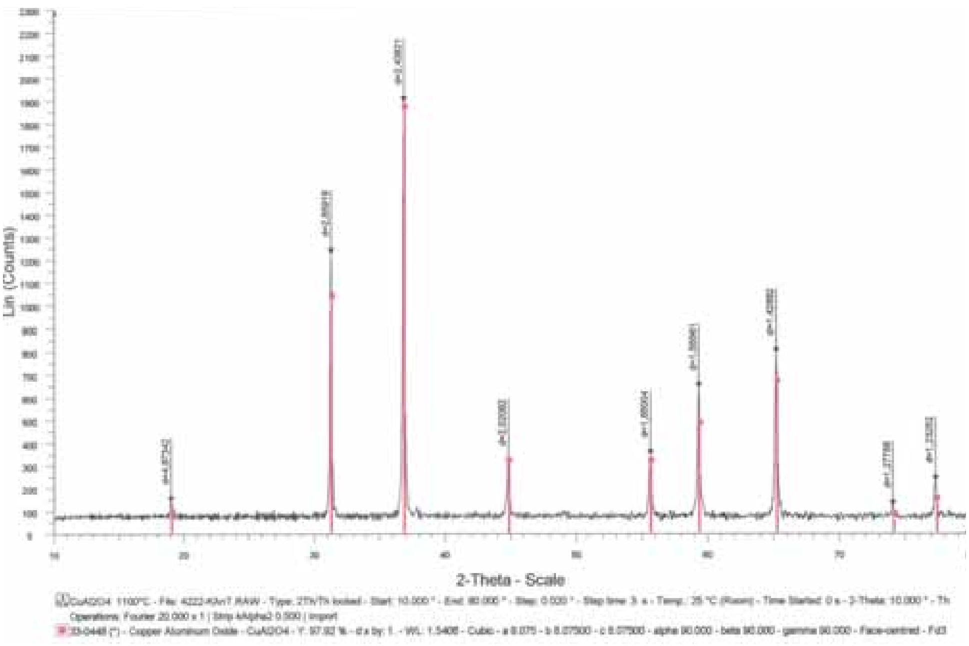

Fig. 2. X-ray diffraction pattern of the $CuAl_2O_4$ pigment (calcination temperature of 1000°C)

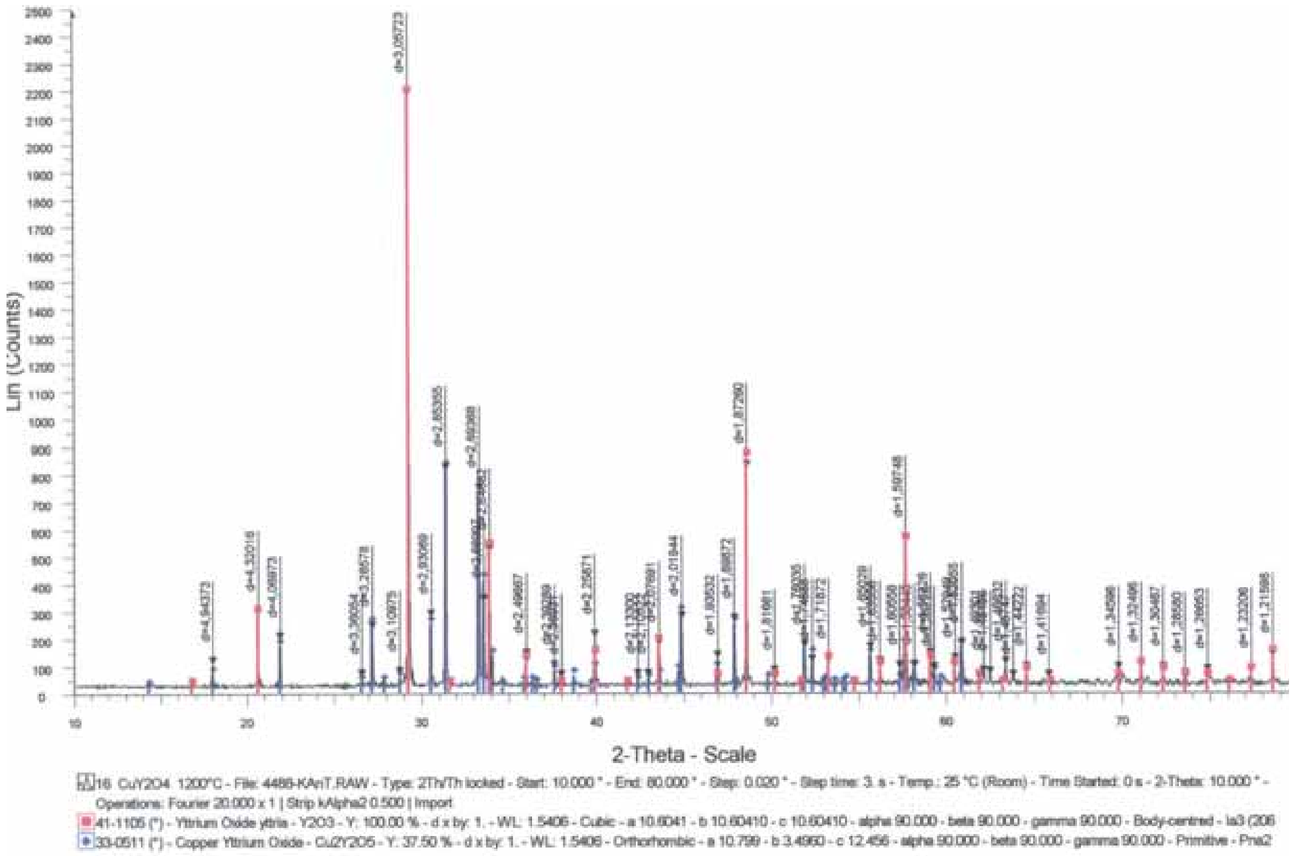

Fig. 3. X-ray diffraction pattern of the CuY_2O_4 pigment (calcination temperature of 1100°C)

The optimal temperature of heating is 1000 and 1100°C. Pigments synthesized at that temperature provide very intensive black colour and the deep and rich turquoise colour hue.

This research has been supported by the Grant Agency of Czech Republic by the grant No. 104/08/0289 and by research plan No. 002 16 275 01.

Literature

[1] Cotton F. A., Willinson G.: Anorganická chemie, Academia, Praha 1973.

[2] Yin X., Han H., Kubo M., Miyamoto A.: Theoretical Chemistry Accounts 109 (2003) 190-194.

[3] Shaheen W. M.: Thermochimica Acta 385 (2002) 105-116.

[4] El-Shobaky G. A., Fagal G. A., Amin N. H.: Thermochimica Acta, 141 (1989) 205-216.

[5] Trojan M., Šolc Z., Novotný M.: Pigments, Kirk-Othmer Encyclopedia of Chemistry Technolgy., Vol. 17, J. Wiley and Sons Inc., New York 1996.

[6] Ishihara S.: Metal Oxides – Chemistry and Applications, Chapt. 7, Taylor and Francis group, Boca Raton 2006.

[7] Kenway P. R., Parker S. C., Mackrodt W. C.: Surface Science 326 (1995) 301-310.

[8] Lee S. B., Chány C. N., Hsieh C. H., Liu C. T.: Physica C 350 (2001) 46-54.

[9] Watanabe T., Sekar C., Shibata H., Matsuda A., Zenitani Y., Akimitsu J.: Physica C 357-360/1 (2001) 380-383.

[10] Kar J. K., Stevens R., Bowen Ch. R.: Journal of Alloys and Compounds 455 (2008) 121-129.

♦