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Synthesis and characterization of $MNd_2W_2O_{10}$ (M = Ni, Cu, Co, Zn) as new ceramic pigments

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Abstract

New compounds based on tungstate were synthesized as environmentally friendly inorganic pigments for ceramic glazes. The pigments have been prepared by means of the solid state reaction. The intermediate compounds MWO_4 were synthesized using two methods of preparation: solid state reaction and precipitation. This work is focused on mixed d-electron metal and neodymium (III) tungstate. The optimum conditions for synthesis of intermediate products MWO_4 (M = Ni, Zn, Co, Cu), Nd_2WO_6 and final products $MNd_2W_2O_{10}$ were determined by TG/DTA analysis of starting mixtures. The thermal stability of $MNd_2W_2O_{10}$ (M = Ni, Zn, Co, Cu) was also determined by TG/DTA methods and by a heating microscope with automatic image analysis. Subsequent research was focused on the influence of d-electron metal tungstates on the colour properties of the $MNd_2W_2O_{10}$ pigments. All samples were found in interesting colour hues that were obtained for Ni – green-yellow and for Zn – light violet, Cu – yellow and Co – blue.

Keywords: Inorganic Pigment, Solid State Reaction, Thermal Analysis, D-electron Metal Tungstate, Neodymium(III) Tungstate

SYNTEZA I CHARAKTERYSTYKA $MNd_2W_2O_{10}$ (M = Ni, Cu, Co, Zn) JAKO NOWYCH PIGMENTÓW CERAMICZNYCH

Zsyntezowano nowe związki oparte na wolframianie jako przyjazne dla środowiska nieorganiczne pigmenty przeznaczone do szkliw ceramicznych. Pigmenty wytworzono w drodze reakcji w stanie stałym. Związki przejściowe MWO_4 zsyntezowano wykorzystując dwie metody: reakcję w stanie stałym i wytrącania. W pracy skupiono się na mieszanym wolframianie metalu d-elektronowego i neodymu(III). Optymalne warunki syntezy produktów przejściowych w postaci MWO_4 (M = Ni, Zn, Co, Cu) i Nd_2WO_6 oraz produktów końcowych — $MNd_2W_2O_{10}$ – określono za pomocą analizy TG/DTA mieszanin wyjściowych. Stabilność cieplną $MNd_2W_2O_{10}$ (M = Ni, Zn, Co, Cu) również określono korzystając z metody TG/DTA oraz mikroskopu grzewczego z automatyczną analizą obrazu. W kolejnych badaniach skupiono się na wpływie wolframianów metalu d-elektronowego na właściwości barwne pigmentów $MNd_2W_2O_{10}$. Wszystkie próbki prezentowały interesujące odcienie kolorów: dla Ni – zielono-żółtego, dla Zn – jasnofioletowego, dla Cu –żółtego i dla Co – niebieskiego.

Słowa kluczowe: pigment nieorganiczny, reakcja w stanie stałym, analiza termiczna, wolframian metalu d-elektronowego, wolframian neodymu(III)

1. Introduction

Nowadays, the solid-state chemistry of mixed-metal oxides containing both rare-earths and d-electron metals has attracted a great deal of interest. These inorganic materials adopt a diverse range of structures and show a wide range of electronic properties. Rare-earth ditungstates are known as promising host materials for luminescent applications [1]. MWO_4 are important materials of the metal tungstate families that have high application potential in various fields, such as in microwave application, optical fibres, scintillating materials, humidity sensors, magnetic properties, catalysis [2, 3] and pigments. Some of them are extensively used as luminescent materials which employ practically any kind of energy as the excitation source [4] and they have been investigated for their optical applications [5, 6].

Depending on the size of a modifier cation, tungstates can crystallize in the form of either scheelite or wolframite. Majority of natural tungsten ores contain the minerals scheelite ($CaWO_4$) and wolframite $(Fe,Mn)WO_4$ [7]. Scheelite structures, where the tungsten atom adopts tetrahedral coordination, are formed when large bivalent cations (Ca^{2+}, Ba^{2+}, Pb^{2+} and Sr^{2+}) are present; in cases of smaller bivalent cations (Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+} and Zn^{2+}), the wolframite structure is formed, where the tungsten atoms adopt an overall six-fold coordination. In addition, the transition from scheelite to wolframite can be stimulated by high pressure: ~1.2 GPa for $CaWO_4$ and 5 GPa for $BaWO_4$ [8, 9].

Most previous approaches to the preparation of these families of compound, e.g. $CoRE_2W_2O_{10}$, $CoWO_4$, RE_2WO_6, $ZnRE_4W_3O_{16}$ etc., used the solid state reaction at a high temperature [1, 10, 11]. Another possibility is to use precipitation or a polymeric precursor method for synthesis of MWO_4 compounds; this way has been used for obtaining e.g. RE_2WO_6 and $CoWO_4$ [5, 12, 13].

In this study, two methods of preparation of MWO_4 (M = Ni, Zn, Co, Cu) were used: solid state reaction and precipitation. The MWO_4 has been used for preparation of final ditungstate pigments of the formula $MNd_2W_2O_{10}$. These compounds represent possible inorganic pigments which

are alternative from the environmental point of view. Thermal analysis (TG-DTA) has been used for determination of optimum synthesis conditions of the pigments. The influence of d-block metal tungstates on the colour properties of the pigments has been investigated as well.

2. Experimental

The pigments of the formula $MNd_2W_2O_{10}$ were prepared by solid state reaction between Nd_2WO_6 and MWO_4 (M = Ni, Zn, Co, Cu). These intermediate compounds were obtained by solid state reaction and by precipitation. Nd_2WO_6 was prepared using the solid state reaction between Nd_2O_3 (98.0%, Bochemie, CZ) and WO_3 (99.9%, Osram, CZ) at high temperatures. The quantity of Nd_2O_3 respect weight changes during storage. Divalent metal tungstates were obtained by calcination of the following mixtures: WO_3+$NiSO_4 \cdot 7H_2O$ (99.0%, Lach-Ner, CZ), WO_3+$CuSO_4 \cdot H_2O$ (99.8%, Lach-Ner, CZ) and WO_3+$ZnSO_4 \cdot 7H_2O$ (99.3% Lach-Ner, CZ). The starting materials were homogenised in a porcelain mortar with a pestle. The reaction mixtures were transferred into a corundum crucible and subjected to calcination at the following stages: 600 °C (6 h), 800 °C (12 h), and 1050 °C (12 h). For the sample $CuWO_4$, the calcination stages were different: 600 °C (6 h), 800 °C (12 h), and 850 °C (12 h).

The second method of preparation of intermediate compounds was precipitation. The desired metal nitrates: $Nd(NO_3)_3 \cdot 6H_2O$ (99.9% Sigma-Aldrich, CZ), $Ni(NO_3)_2 \cdot 6H_2O$ (99.9% Lach-Ner, CZ), $Cu(NO_3)_2 \cdot 3H_2O$ (99.8% Lachema, CZ), $Zn(NO_3)_2 \cdot 6H_2O$ (98.0% Lachema, CZ), $Co(NO_3)_2 \cdot 6H_2O$ (99.0% Lachema, CZ) were individually dissolved in distilled water. The metal nitrate solution (0.05 M, 250 ml) was poured into the equal volume of an aqueous solution (0.05 M) of sodium tungstate $Na_2WO_4 \cdot 2H_2O$ (99.0%, Penta, CZ), maintaining stoichiometric ratio of 1:1. The solutions were subsequently mixed with a magnetic stirrer for 5 minutes. The precipitated metal tungstates $MWO_4 \cdot xH_2O$ (M = Ni, Zn, Co, Cu) were collected by filtration and were thoroughly washed with deionized water and dried at 90 °C.

The final pigments ($MNd_2W_2O_{10}$) were prepared by using the mixtures of Nd_2WO_6 with MWO_4 at the molar ratio of 1:1. The Nd_2WO_6+MWO_4 (M = Ni, Zn, Co) mixtures were calcinated at the following stages: 900 ºC (12 h), 1000ºC (12 h), 1050 ºC (12 h), and 1080 ºC (2 × 12 h) in an electric furnace with a heating rate of 10 ºC·min^{-1}. For preparation of $CuNd_2W_2O_{10}$, the calcination stages were as follows: 750 °C (12 h), 800 °C (12 h), and 850 °C (2 × 12 h). After each period of heating, the samples were gradually cooled to the ambient temperature and homogenised by grinding.

For testing in ceramic glazes, aqueous suspensions containing 10 mass% of the pigment and 90% of frit were prepared by hand milling. The frit contained a lustrous colourless glaze, which was the lead ceramic glaze composed of 51% of PbO (G028 91, Glazura, CZ) with the value of a thermal expansion coefficient being $\alpha_{20\text{-}500\,°C} = 79.0 \cdot 10^{-7}$ K^{-1}. The second type of colourless glaze (a white opaque zirconium leadless glaze, Pw141 91, Glazura, CZ) with $\alpha_{20\text{-}500\,°C} = 59.5 \cdot 10^{-7}$ K^{-1} was also used as the frit. The slurries were deposited on ceramic shards. The samples with the first and second type of glazes have been fired for 15 min at a temperature of 880 °C and 980 °C, respectively.

The formation of the new neodymium pigments $MNd_2W_2O_{10}$ and of the intermediate compounds MWO_4 and Nd_2WO_6 was followed by thermal analysis using an STA 449C Jupiter (NETZSCH, Germany) equipment with simultaneous registration of TG and DTA curves. The measurements were carried out in open ceramic crucibles in a temperature range of 30–1100 °C or 30–1200 °C with the temperature increase of 10 °C·min^{-1} in air; α–Al_2O_3 was used as a temperature stable standard. The formation temperatures of final products $MNd_2W_2O_{10}$ from intermediate products prepared by solid state synthesis have been previously reported [11].

The thermal stability of the pigments was also studied using a heating microscope with automatic image analysis (Hesse Instruments, Germany). The powders were formed into pellets for these measurements. A heating rate was 10 °C·min^{-1}.

Phase composition of the pigments was studied using X-Ray diffraction analysis. Diffractograms of the samples were measured by a D8 diffractometer (Bruker, GB) in the 2θ range of 10–80°; $CuK\alpha_1$ (λ = 0.15418 nm) for 2θ < 35°, $Cu\text{-}K\alpha_2$ (λ = 0.15405 nm) for 2θ > 35°, and a scintillation detector were used.

The colour properties of all prepared pigments were objectively evaluated by measuring the spectral reflectance with a ColorQuest XE spectrophotometer (HunterLab, USA). The measurement conditions were as follows: D65 illuminant, 10° complementary observer and measuring geometry d/8°. For the description of colour, the CIE *L*a*b** colour space was used. The *L*a*b** colour space is presently one of the most popular colour space descriptions of object colour and it is widely used virtually in all fields of applications. In this colour space, *L** indicates the lightness, and *a** and *b** are the chromaticity coordinates. The value *C* (Chroma) represents the saturation of the colour and it is calculated according to the equation:

$$C = (a^{*2} + b^{*2})^{1/2} \quad (1)$$

The colour hue of pigments can be also expressed as a hue angle *H*° calculated as follows:

$$H° = arctg\,(b^*/a^*) \quad (2)$$

The hue angle *H*° is defined as starting at the +*a** axis and expressed in degrees; 0° is red (+*a**), 90° is yellow (+*b**), 180° is green (–*a**), and 270° is blue (–*b**).

3. Results and Discussion

Fig. 1 shows TG/DTA curves of amorphous product of precipitation in case of the $ZnWO_4$ preparation as a typical representative. The endothermic peak with the minimum at 167ºC corresponds to the removal of water. The 10.2% mass loss corresponds approximately with 2 molecules of water. The exothermic peak at 376 °C corresponds to the crystallization of monoclinic $ZnWO_4$ from the amorphous form [12]. The dehydration and crystallization temperatures for other MWO_4 (M = Zn, Co, Cu) prepared by precipitation are shown in Table 1.

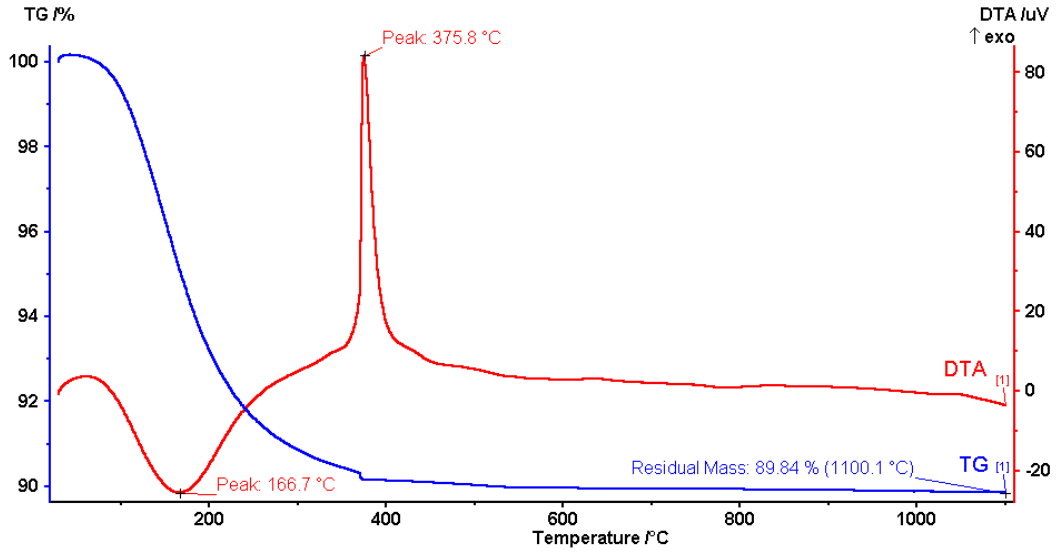

Fig. 1. TG-DTA curves of $ZnWO_4$ precipitate; mass of sample: 311.60 mg, atmosphere: air, heating rate: 10 °C min^{-1}.

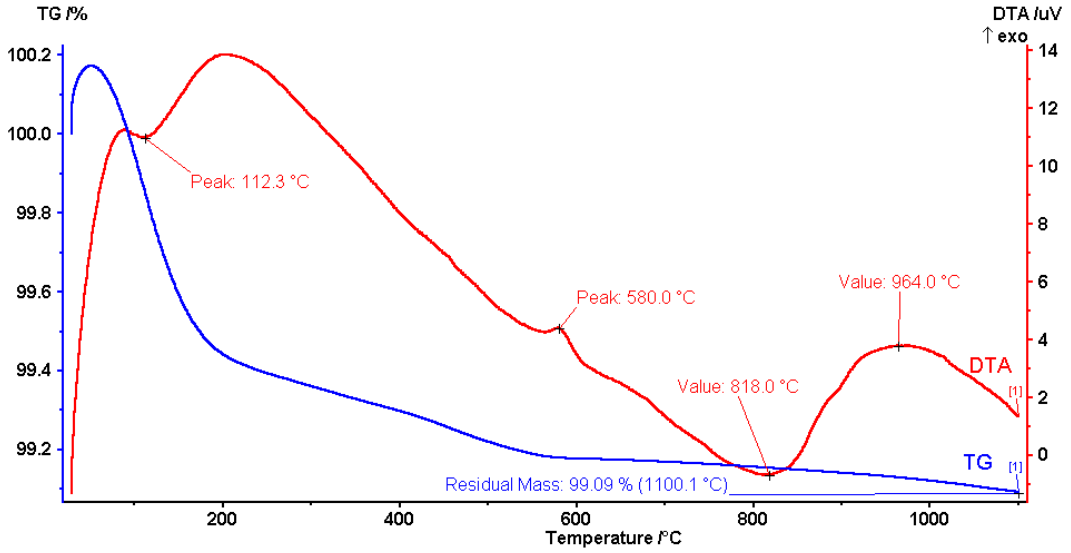

Fig. 2. TG-DTA curves of Nd_2WO_6 precipitate; mass of sample: 295.20 mg, atmosphere: air, heating rate: 10 °C min^{-1}.

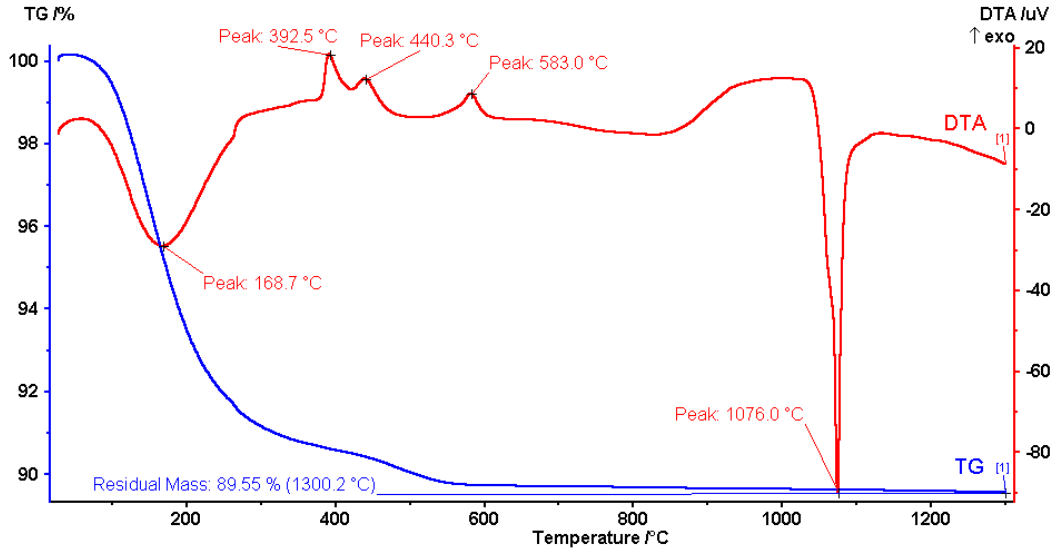

Fig. 3. TG-DTA curves of $ZnNd_2W_2O_{10}$ obtained from MWO_4 reaction mixture prepared by precipitation; mass of sample: 161.60 mg, atmosphere: air, heating rate: 10 °C min^{-1}).

Table 1. Thermal analysis data of $MNd_2W_2O_{10}$ (M = Ni, Co, Cu) reaction mixtures (intermediate products prepared by precipitation).

Compound	Temperature of effect [°C]	Effect	Comments
$CuNd_2W_2O_{10}$	167	endo	dehydration of $CuWO_4$
	425	exo	crystallization of $CuWO_4$
	583	exo	crystallization of Nd_2WO_6
	870	endo	decomposition and melting
$CoNd_2W_2O_{10}$	166	endo	dehydration of $CoWO_4$
	409	exo	crystallization of $CuWO_4$
	440	exo	formation of intermediate product
	582	exo	crystallization of Nd_2WO_6
	1128	endo	decomposition and melting
$NiNd_2W_2O_{10}$	167	endo	dehydration of $CuWO_4$
	495	exo	crystallization of $CuWO_4$
	574	exo	formation of intermediate product
	609	exo	crystallization of Nd_2WO_6
	1124	endo	decomposition and melting

TG/DTA curves of Nd_2WO_6 prepared by precipitation are shown in Fig. 2. In the temperature interval from 100 °C to 600 °C, significant mass loss occurs, corresponding to release of surface adsorbed water. The exothermic peak of the Nd_2WO_6 crystallization with a maximum at 580 °C is registered. Fig. 3 shows the TG/DTA curves for the $ZnNd_2W_2O_{10}$ preparation using the intermediate compounds $ZnWO_4$ and Nd_2WO_6 prepared by precipitation. The thermal dehydration occurred in one step. This fact is indicated with the endothermic peak with a minimum at 169 ºC which is accompanied by a mass change on the TG curve. The exothermic effects with the temperature maxima at 393 °C and 583 °C were associated with crystallization as mentioned in previous paragraphs. The exothermic peak at 440 °C corresponds to the formation of intermediate product $Nd_2W_2O_9$. The endothermic peak with a minimum at 1076 °C is connected with the decomposition and melting of the product. Table 1 shows temperatures of significant peaks for other final pigments obtained using the intermediate compounds prepared by precipitation. The description of DTA/TG curves for the intermediate products by solid state synthesis is reported in ref. [11].

Table 2. Thermal stability of $MNd_2W_2O_{10}$ (M = Zn, Co, Cu) as a function of synthesis method of intermediate compounds: precipitation – PR, solid state reaction – SS.

Sample	Temperature of $MNd_2W_2O_{10}$ decomposition [°C]	
	SS	PR
$ZnNd_2W_2O_{10}$	1085	1030
$NiNd_2W_2O_{10}$	1170	1098
$CoNd_2W_2O_{10}$	1160	1080
$CuNd_2W_2O_{10}$	940	920

The thermal stability verification of the prepared pigments was carried out using the heating microscope. Table 2 shows the values of the decomposition temperature of the $MNd_2W_2O_{10}$ compounds which were prepared using the intermediate compounds, coming from the precipitation or solid state reaction. The heating microscope analyses a silhouette of the prepared pigments and their altering shapes and dimensions over a defined temperature range. The temperature of decomposition was set as the onset of an effect on recorded curves.

The prepared $MNd_2W_2O_{10}$ pigments were subjected to X-ray diffraction analysis. All prepared compounds have the crystalline character. The results of the XRD analysis of $CoNd_2W_2O_{10}$ are shown in Fig. 4. Only during the solid state synthesis, the desired ditungstate product is formed. On the other hand, the products of the precipitation method are composed of several phases, probably as a result of formation of stable intermediates during the synthesis.

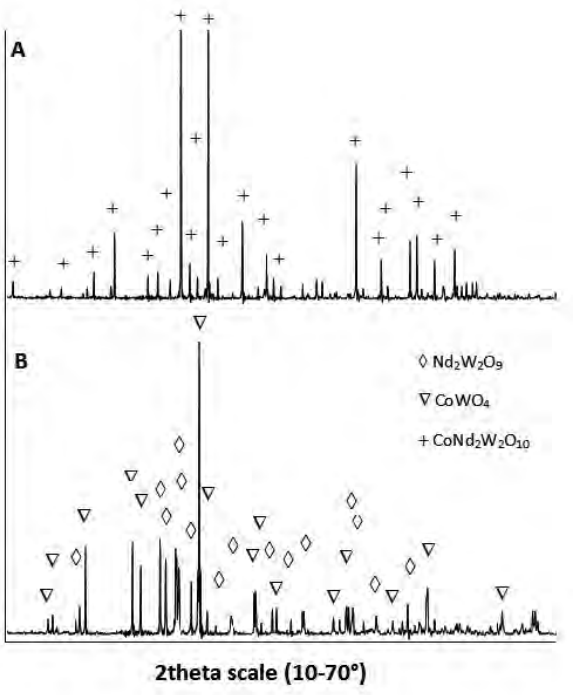

Fig. 4. X-ray diffraction patterns of $CoNd_2W_2O_{10}$ prepared by solid state reaction (A) and precipitation (B).

Table 3. Colour properties of $MNd_2W_2O_{10}$ (M = Ni, Zn, Co) pigments applied into ceramic glaze.

Sample	Using MWO_4 SS; glaze G028 91			Using MWO_4 PR; glaze G028 91			Using MWO_4 SS; glaze Pw141 91			Using MWO_4 SS; glaze Pw141 91		
	*L**	*C*	*H°*	*L**	*C*	*H°*	*L**	*C*	*H°*	*L**	*C*	*H°*
$NiNd_2W_2O_{10}$	57.28	21.23	77.27	72.39	26.18	85.97	83.16	5.62	88.98	81.31	7.38	81.81
$ZnNd_2W_2O_{10}$	72.72	4.50	21.26	77.49	7.88	78.66	87.23	5.20	287.70	87.79	4.97	284.46
$CoNd_2W_2O_{10}$	37.93	9.04	270.95	39.10	24.27	286.81	65.93	9.54	261.50	69.42	16.85	270.51
$CuNd_2W_2O_{10}$	63.17	25.08	186.25	68.63	21.51	179.65	77.92	12.70	190.98	83.19	10.76	200.74

In Table 3, colour parameters of all samples applied into the ceramic glazes are summarised. The glass surfaces of all applications prepared from final pigments are very high quality and the colours are intensive, especially when using the first type of glaze. The colour of these applications varies only slightly depending on the method of preparation of the intermediate compounds. Pigments made from the precipitated intermediates had to be milled. Their colour has changed only slightly due to the milling.

As already described, pigments applied to the first type of glaze, which was the lead ceramic glaze containing 51% of PbO, had intensive colours. The hue of $NiNd_2W_2O_{10}$ varies from light yellow to dark yellow depending on the method of preparation of $NiWO_4$. The $NiNd_2W_2O_{10}$ pigment obtained using $NiWO_4$ SS (prepared by solid state reaction) has lower values in all measured colour properties as opposed to the other pigment, $NiNd_2W_2O_{10}$ obtained using $NiWO_4$ PR (prepared by precipitation). The value of *L** is significantly higher, the value of *C* is slightly higher and the final pigment is brighter. A significant change of hue values was observed in the $ZnNd_2W_2O_{10}$ pigment depending on the method of preparation of the intermediates. This trend was not observed in the brightness and saturation. The colour of $ZnNd_2W_2O_{10}$ is light pink. For the $CoNd_2W_2O_{10}$ pigment, obtained from the intermediate compounds prepared using two methods, the difference is primarily in values of chroma; the depth of shade is higher for $CoNd_2W_2O_{10}$ prepared from $CoWO_4$ PR; the differences of the *L** values are insignificant. The hue of $CoNd_2W_2O_{10}$ ranges from dark blue to ocean blue. The colour of $CuNd_2W_2O_{10}$ is light green. A more satisfactory hue was achieved in $CuNd_2W_2O_{10}$ prepared by using $CuWO_4$ SS. The differences of the *L** and C values are insignificant in the $CuNd_2W_2O_{10}$ pigments depending on the method of preparation of the intermediates.

As the second type of glaze was white opaque zirconium leadless glaze, the hue has been brightening. All measured parameters differed only slightly. The colour hue did not differ with reference to the method of preparation of intermediate compounds.

4. Conclusions

The aim of the present work was to synthesize new ceramic pigments based on neodymium tungstates with d-electron metal as a colouring agent. The pigments were synthesized using a conventional ceramic method, i.e. solid state reaction synthesis. The intermediate compounds, namely Nd_2WO_6 and MWO_4 (M = Zn, Co and Cu), were prepared by two different methods. The first one included a solid state reaction, and the second was precipitation.

TG/DTA methods were used to study processes during the preparation of final pigments. It has been observed that the formation of intermediate compounds (MWO_4) originated from the precipitation method occurred at lower temperatures than the formation of intermediate compounds prepared by the solid state reaction method. However, the results of X-ray diffraction analysis showed that the process of crystallization of MWO_4 prepared by the precipitation was significantly more difficult: initially, it produced compounds in the amorphous form, and then crystallization occurred; moreover, these compounds had lower thermal stability.

The colour properties of final pigments were measured. The pigments of the $MNd_2W_2O_{10}$ (M = Ni, Zn, Co and Cu) formula were applied into two types of glazes. The colour of final pigments was different with respect to the preparation method of the MWO_4. The hue of $NiNd_2W_2O_{10}$ varied from light yellow to dark yellow. The colour of $ZnNd_2W_2O_{10}$ was light pink. The hue of $CoNd_2W_2O_{10}$ ranged from dark blue to ocean blue.

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