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The vast colour spectrum of ternary metal oxynitride pigments

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Abstract

Ternary metal oxynitrides have attracted considerable attention because of their bright colouring, while oxide perovskites are usually colourless. In this report some technically relevant properties for the application of these materials as pigments, such as colour and thermal stability, have been measured. The crystal structure and phase purity of the samples were analysed by X-ray diffraction. The accurate colours were determined using a colorimeter. The selected oxynitrides possess a variety of different colours like yellow, orange, red, brown, green and black. In addition, the thermal stability of the compounds was investigated. All studied samples are stable in air, water and diluted acids at room temperature and start to decompose in air only above 400 °C. This high thermal and chemical stabilities make oxynitrides promising candidates to be employed in rubbers, thermoplastics, paints, etc. as ceramic pigments to substitute dyes, which contain toxic metals.

Keywords: Oxynitride perovskites; Colorimetric measurement; Thermal stability; Non-toxic pigments

1. Introduction

In the last years, most of the developed countries have created rules restricting the use of pigments that contain toxic elements and/or heavy metals (e.g. Cd, Cr, Pb, Sb) to protect human health and the environment. It is a big challenge to develop new inorganic pigments that are non-toxic and environmental friendly [1–3]. A number of scientists are working in this field and various interesting approaches have been published. For example, Calbo et al. minimised the Cr content and partially substituted Ni by Mg and Zn in the spinel type black pigment $Ni(Fe, Cr)_2O_4$ [4]. Fores et al. obtained the pigment $Co_{0.05}Zn_{1.95}SiO_4$ with an intense blue colour, which contains only 2.5% mol of cobalt [5]. Furthermore, Munoz et al. minimised the amount of Cr in the green pigment formulation $Cr_{1.14}Al_{0.86}O_3$ [6].

Following the necessity to develop eco-friendly dyes and pigments, oxynitrides are good candidates, since they show bright colours and do not contain toxic heavy metals [7–10].

Pérez-Estébanez et al. studied the fluorite-type oxynitride Zr–Ln–O–N (Ln = Ce, Eu and Er). The pigments based on europium were white, while the ones based on erbium showed a pink colour. The compounds with cerium are orange and green, depending on the doping amount. They exhibit good colour properties such as intense colouration and high reflectance [11].

The optical properties of the oxynitride solid solution GaN:ZnO were investigated by Maeda et al. They found that these materials have yellowish colour. The $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ compounds have smaller band gap values than the pure end members GaN and ZnO. The samples have their absorption edges shifted to longer wavelengths when x (Zn content) increases [12].

The system $Ta_{(3-x)}Zr_xN_{(5-x)}O_x$ was studied by Guenther and Jansen. Pure Ta_3N_5 is dark red and with the introduction of Zr^{4+}/O^{2-} in the crystal lattice the compounds start presenting orange and yellow colours. By substituting the ''softer''

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nitrogen atoms for the ''harder'' oxygen atoms, the band gap increases and the colour is shifted from red to yellow [13].

In recent years, oxynitrides based on the perovskite framework have been investigated, too. For example, Jansen and Letschert reported on the solid solution $Ca_{(1-x)}La_xTaO_{(2-x)}N_{(1+x)}$. They demonstrated that changes in the x values result in compounds with yellow, orange and red colours. With this innovative discovery the reddish pigments based on the problematic element cadmium may now possibly be substituted [14].

Lately we reported on a soft chemistry synthesis method for oxynitrides of the ABO_2N type ($A = Ca^{2+}$, Sr^{2+}, Ba^{2+} and $B = Ta^{5+}$, Nb^{5+}). The compounds exhibited different colours like yellow, orange, ochre and black. Specimens with the same chemical composition did not show significant differences in colour indicating that the preparation technique has little influence on the optical properties [15]. These investigations motivated us to start a more general survey on the colour spectrum of perovskite-related oxynitrides.

In this report it will be demonstrated that changes in the cationic composition of complex oxynitrides result in different colours that cover a vast range of the visible light spectrum. This colour flexibility makes oxynitrides a promising class of ceramics for the production of pigments without toxic elements.

2. Materials and methods

2.1. Reagents and chemicals

For the synthesis of the studied oxynitride perovskite the following reagents were used: $Ca(NO_3)_2\cdot 4H_2O$ (p.a. – Fluka), $Sr(NO_3)_2$ (p.a. – Fluka), $Ba(NO_3)_2$ (99% – Aldrich), $NbCl_5$ (98% – Riedel-de Haen), $La(NO_3)_3\cdot 6H_2O$ (p.a. – Fluka), $TaCl_5$ (p.a. – Merck), $ZrC_{12}H_{28}O_4$ (70 wt% solution in 1-propanol – Aldrich), $Yb(NO_3)_3\cdot 5H_2O$ (p.a. – Serva), $TiC_{12}H_{28}O_4$ (97% – Aldrich) and citric acid (99% – Fluka).

2.2. Synthesis of oxide precursors

Amorphous oxide powders were synthesised by a polymeric-precursor route [15]. This synthesis method consists basically of dissolving stoichiometric quantities of the desired cations (as nitrates, chlorides or isopropoxides) in an aqueous polymeric solution, e.g. citric acid solution. For the chlorides $TaCl_5$ and $NbCl_5$, it is necessary to dissolve them in a solution of anhydrous citric acid and dry ethanol, in order to avoid the formation of oxide/hydroxide precipitation. Typically, the solution is stirred at ca. 70 °C for several hours, the solvent is evaporated and the solution becomes a gel. To get the white and amorphous oxide powders from these gels, the organic matrix is burned at around 650 °C for 2 h. This technique has the advantage to produce homogeneous oxides and it decreases the necessary time and temperature of synthesis [16].

2.3. Ammonolysis

The amorphous oxide powders were placed in alumina crucibles and ammonolysed in a tube furnace with an NH_3 flow of 50–150 ml/min to result in well-crystallised oxynitrides. Different heating temperatures and reaction times were necessary to produce the diverse oxynitride compounds as listed in Table 1.

2.4. Characterisation

The crystal structure and phase purity of the powders were investigated by X-ray diffraction using a Seifert θ/θ 3000, diffractometer operating with Cu Kα radiation. A $\theta/2\theta$ scan was performed in the angular range 10°–60° with an increment of 0.02° and a counting time of 1 s per data point. The CIELAB colour parameters of the different samples were measured at room temperature using a Gretag Macbeth colorimeter model Color-Eye 2180. The thermal stability of the compounds was studied by thermogravimetry, using a Netzsch thermobalance

Table 1
Temperature and time of ammonolysis, colour and corresponding space group for each studied sample

Sample	T (°C)	Time (h)	Colour	Crystal system	Space group	Cell parameters
$CaTaO_2N$	950	18	Yellow	Orthorhombic [24]	Pnma	$a = 5.6239$, $b = 7.8954$, $c = 5.5473$
$SrTaO_2N$	950	18	Orange	Tetragonal [24]	$I4$/mcm	$a = 5.7049$, $c = 8.0499$
$BaTaO_2N$	1000	54	Red	Cubic [25]	$Pm\bar{3}m$	$a = 4.1125$
$Yb_2Ta_2O_5N_2$	950	72	Dark green	Cubic [26]	$Fd\bar{3}m$	$a = 10.235$
$CaZr_{0.5}Ta_{0.5}O_{2.5}N_{0.5}$	950	108	Ochre	Orthorhombic [27]	Pnma	$a = 5.5780$, $b = 7.9550$, $c = 5.6840$
$SrNbO_2N$	950	54	Brown	Tetragonal [28]	$I4/mcm$	$a = 5.7056$, $c = 8.1002$
$BaNbO_2N$	950	72	Black	Cubic [25]	$Pm\bar{3}m$	$a = 4.1285$
$SrTiO_3$:N	1000	48	Light blue	Cubic [29]	$Pm\bar{3}m$	$a = 3.9050$
$LaTiO_2N$	1000	24	Brown	Triclinic [30]	$I\bar{1}$	$a = 5.6097$, $b = 7.8719$, $c = 5.5752$

(STA 409) in the temperature range from 25 to 1200 °C with a heating rate of 10 °C/min in synthetic air atmosphere.

3. Results and discussion

3.1. X-ray analysis

Except for $Yb_2Ta_2O_5N_2$, which has a fluorite-type structure, all the synthesised samples showed well-defined perovskite structures without preferential orientation, as displayed in Fig. 1. The diffraction peaks could be indexed according to the respective space groups listed in Table 1. Impurities were only found for $CaTaO_2N$, which shows a small quantity (<1%) of $TaO_{1.6}$ as second phase.

3.2. Colorimetry analysis

The samples' colour parameters are plotted in Fig. 2. The axes in the 3D graphic are a^* (−) green, (+) red, b^* (−) blue (+) yellow and L^* (0) dark/black (100) light/white. The colours shown in the plot correspond to the respective $a^*b^*L^*$-values of each sample. It is important to note that the different specimens show a big variety of colours as yellow, ochre, orange, red, green, light blue, brown, and black.

In Ref. [14] it was demonstrated how a simultaneous exchange of Ca^{2+}/O^{2-} by La^{3+}/N^{3-} influences the colour of perovskite oxynitrides. To extend these investigations, we have also studied samples with the same nitrogen stoichiometry in order to investigate how modifications in the cationic sublattice control the pigment colour.

Comparing the samples with the general composition ABO_2N, one can see that changes on the cationic sites of the oxynitride perovskites result in major colour variations. For example, in the tantalum oxynitrides $ATaO_2N$, the exchange of the A cation by another with the same formal charge (+2) leads to the following colours: $BaTaO_2N$ is red, $SrTaO_2N$ is orange, and $CaTaO_2N$ is yellow. This colour change is correlated with a reduction of crystallographic symmetry. While

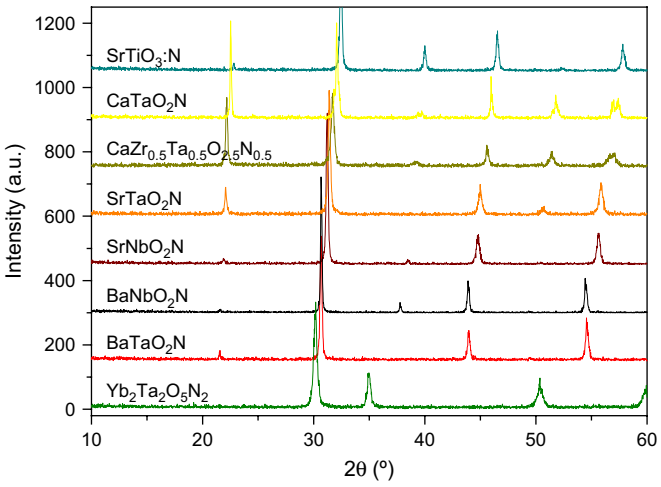

Fig. 1. X-ray diffraction pattern of some studied oxynitrides.

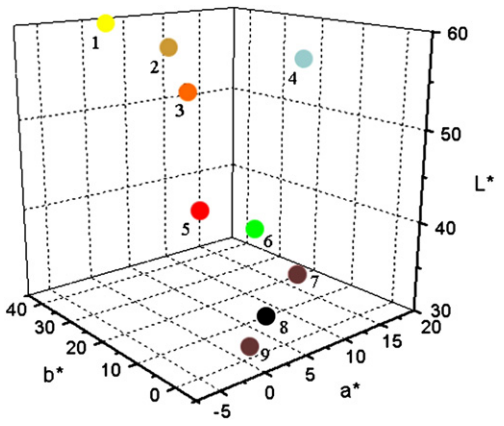

Fig. 2. Colorimetric graphic of some oxynitride perovskite pigments: (1) $CaTaO_2N$, (2) $CaZr_{0.5}Ta_{0.5}O_{2.5}N_{0.5}$, (3) $SrTaO_2N$, (4) $SrTiO_3$:N, (5) $BaTaO_2N$, (6) $Yb_2Ta_2O_5N_2$, (7) $LaTiO_2N$, (8) $BaNbO_2N$ and (9) $SrNbO_2N$.

$BaTaO_2N$ is cubic, the symmetry is reduced to tetragonal for $SrTaO_2N$ and finally $CaTaO_2N$ possess an orthorhombic unit cell. These crystallographic changes are common for perovskites and account for the smaller size of the A cation. The ionic radii of the A cation surrounded by 12 ions are 1.48 Å, 1.58 Å and 1.75 Å for Ca^{2+}, Sr^{2+} and Ba^{2+}, respectively [17]. Table 1 gives the cell parameters of these compounds. The reduced radius of the A cation leads to a shrinking of the averaged cell parameters of 4.111 Å, 4.034 Å, and 3.947 Å for A = Ba^{2+}, Sr^{2+} and Ca^{2+}, respectively. It is important to note that, on the other hand, the tantalum–oxygen/nitrogen distances remain almost constant for these three compounds. In contrast to the bond lengths, the bond angles Ta–(O,N)–Ta strongly alter with the size of the A cations. The angles for the respective compounds are 180°, 169.9°, and 153.3°. The change in bond angles results in modifications of the overlap between the O/N-p and the metal-d orbitals, both for σ- and π-type bonds. A better overlap, i.e. bond angles closer to 180° is expected to result in a more covalent character of the transition metal–oxygen bond and in turn leads to a smaller band gap.

It has lately been demonstrated both on the basis of experimental results and DFT calculations that the charge and electronegativity of the A cations have a negligible impact on the electronic structure of perovskite-related oxides with d^0 configuration [18]. In contrast, a size mismatch of the A cation can trigger a structural distortion, resulting in a reduced bond angle value smaller than the 180° in the cubic perovskites. These smaller bond angles strongly influence the conducting band, which consists of antibonding π* orbitals with dominating metal-d character. While the energetic position of the centre of the conducting band remains almost unchanged, a reduced angle leads to a smaller band *width*, in turn increasing the band gap as schematically shown in Fig. 3. Reported band gap values for $ATaO_2N$ of 1.8 eV, 2.1 eV and 2.4 eV for A = Ba, Sr, and Ca, respectively, strongly support these considerations [19].

Another possibility to alter the colour of oxynitrides is the substitution of the B cation by another possessing the same

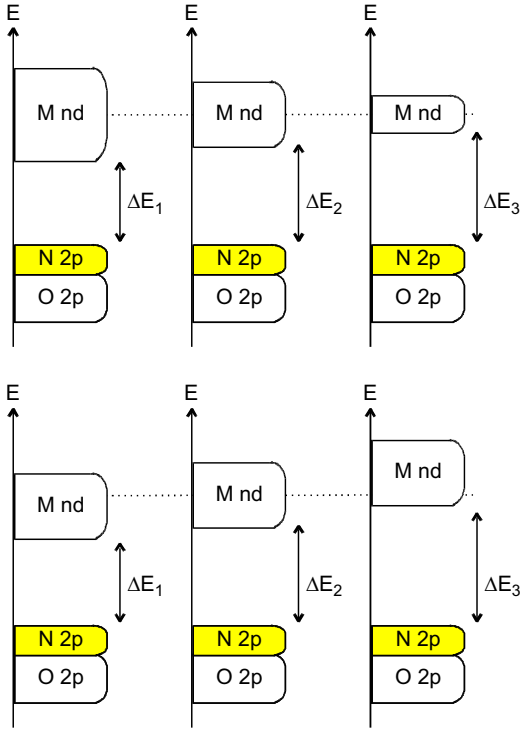

Fig. 3. Schematic sketch of the influence of B–O–B bond angle (top) and electronegativity of the B cation (bottom) on the optical band gap in oxynitride perovskites. The valence band (VB) consists of non-binding O/N 2p orbitals and therefore remains basically unchanged. Due to the lower electronegativity of nitrogen the N 2p orbitals have a higher energy than the O 2p orbitals, explaining the lower band gaps of oxynitrides with respect to their corresponding oxides. A decreasing bond angle (top row) decreases the width of the conducting band (CB) and in turn increases the band gap while leaving the energetic centre of the CB unchanged (dotted line). In contrast, a decreasing electronegativity of the B cation (bottom row) increases the energy of the CB while barely affecting its width.

formal charge. Good examples are the perovskite oxynitrides ABO_2N with pentavalent B cations. While $SrTaO_2N$ is orange, $SrNbO_2N$ has a brown colour while $BaTaO_2N$ is red and $BaNbO_2N$ black. For the respective niobates the absorption edge shifts to longer wavelengths compared to the tantalates, i.e. they have narrower band gaps. This effect cannot be explained by atomic bond distance values, because Nb^{5+} has the same ionic radius (0.88 Å) as Ta^{5+} in an octahedral coordination. The observed change in colour can also not be elucidated by crystal symmetry, since both the Sr-compounds are tetragonal and both the Ba-compounds are cubic. The observed colour changes most likely originate from different electronegativities of the B cations. For a more electronegative transition metal ion the corresponding t_{2g}-orbitals (which mainly contribute to the conducting band) are closer to the anionic 2p orbitals leading to both narrower band gaps and more covalent B–O bonds.

This assumption can be confirmed by comparing the ionicity of the atomic bonds for the different compounds. The ionicity of Ta–O and Nb–O bonds can be calculated using Pauling's formula: $I = 1 - \exp[-(\chi_a - \chi_b)/4]$, where χ_a and χ_b indicate the electronegativities of the cation and anion, respectively [20]. The obtained ionicity values using Pauling's electronegativities are $I_{Ta-O} = 0.610$ and $I_{Nb-O} = 0.571$. The niobium–oxygen bond is therefore less ionic (more covalent) resulting in an absorption at longer wavelengths compared to the respective tantalate compounds. This simple scenario has lately been confirmed for pure oxides possessing perovskite-related structures by band structure calculation [18]. The influence of different electronegativities of the B cations is schematically displayed in the lower part of Fig. 3. The choice of B cation has a minor effect on the width of the conducting band but strongly influences its energetic position, resulting in a strong decrease of the band gap with increasing covalence/electronegativity of the B cation.

3.3. Thermogravimetric analysis

Because pigments may be exposed to elevated temperatures during their application, it is important to know the temperature at which the corresponding compounds start to decompose. At room temperatures all oxynitride samples were found to be stable in air and moist atmosphere. When heated in a thermobalance to high temperatures under synthetic air all compounds showed a similar behaviour as can be seen in Fig. 4. Between room temperature and approximately 400 °C a small reduction of weight is observed, resulting from the loss of adsorbed water. This effect is most obvious for $LaTiO_2N$ and by far less pronounced for the other compounds. The loss of water is followed by a strong increase in weight. This increase is considerably higher than the expected value for the reaction $2ABO_2N + 1.5O_2 \rightarrow 2ABO_{3.5} + N_2$. After reaching a maximum the sample weights slowly redecrease in a region of a few hundred degree Celsius. Finally, a sharp weight loss is observed and the oxides $ABO_{3.5}$ are formed. A number of studies have been performed to explain the unexpected intermediate weight gain during oxidation. It was found that some nitrogen stays retained in the completely oxidised structure, forming intermediate dinitrogen-containing compounds as B···N≡N and B···N≡N···B or metal–nitrogen intermediate compounds as B≡N [21–23]. On the other hand, thermogravimetric measurements

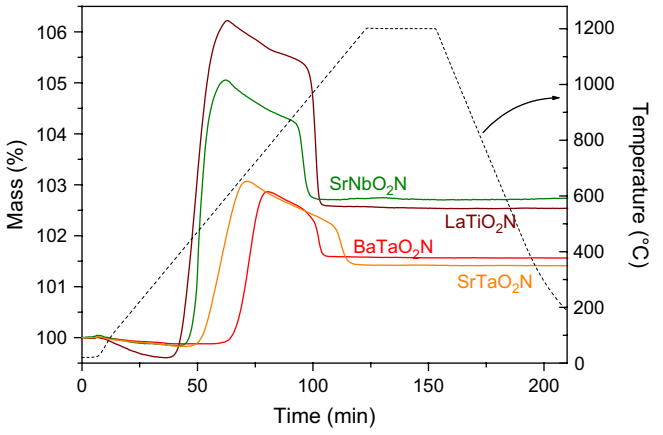

Fig. 4. Thermogravimetric analysis of $SrNbO_2N$, $LaTiO_2N$, $BaTaO_2N$ and $SrTaO_2N$.

coupled with mass spectroscopy revealed that already during the weight increase considerable amounts of N_2 are released [15]. At higher temperatures nitrogen is completely detached and the weight decreases to its final value.

The temperature at which the oxynitrides start to decompose/oxidise (i.e. the samples' weight starts to increase) varies among the different compounds. As an example, $LaTiO_2N$ starts to decompose already at 350 °C, while $SrNbO_2N$ is stable up to 410 °C and $BaTaO_2N$ starts to decompose at 580 °C. As mentioned above, the knowledge on the thermal stability is essential because for a number of applications the pigments are exposed to heating treatments. The decomposition temperature is useful to decide whether a pigment can be applied, for example as colourants for papers, thermoplastics, rubbers, ceramics, enamels, etc.

4. Conclusion

Oxynitride perovskites show a large range of colours and are stable in air, water or diluted acids at room temperature. They also have the advantage of not containing toxic metals and, in turn, are eco-friendly. Thermogravimetric analysis revealed very high temperature stability. Some of the oxynitride perovskites are stable in synthetic air even up to 580 °C. Oxynitride-based dyes therefore have the potential to be employed as colouring agents for fibres, paints, plastics, and medium-temperature ceramics, substituting toxic pigments. The exchange of cations results in strong changes in the colours of the respective compounds, opening the possibility to fine-tune the colour by doping with small amounts of different cations.

Based on very simple consideration, a systematic model for changes in the energetic position of the conducting band can be derived. Starting from a given material the band gap can be decreased by increasing the crystallographic symmetry (e.g. by adjusting the size of the A cation) or by increasing the electronegativity of the involved B cation. These relationships open the possibility to tailor the optical band gap of oxynitride perovskites. In addition, the isoelectronic replacement of A^{2+}/O^{2-} by Ln^{3+}/N^{3-} (Ln being a lanthanide ion) strongly alters the electronic properties by changing the density of states in the valence band. With these different parameters at hand, the colour of oxynitrides can effectively be modified and dyes of various colours are likely to be accessible in the near future.

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