

STUDY OF PEROVSKITE COMPOUNDS

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Perovskites belong to the great group of the inorganic pigments and thanks to their excellent properties they have been widely used in an industry. CaTiO_3 , BaTiO_3 and SrTiO_3 with the perovskite structure were prepared in this work. These compounds were synthesized with using the solid state reaction by calcination in temperature region 1000–1200°C. The thermal analysis was used for characterization of thermal behaviour and formation of tested perovskites. The main aim of this work was studied the influence of calcination temperature on colour properties of perovskites. Colour properties of powdered compounds and samples applied into ceramic transparent glaze P 07491 were also studied. The tested compounds can be described by different light colour hues and that depending on calcining temperature. The structures of the powdered compounds were studied by X-ray diffraction analysis.

Keywords: inorganic pigments, optical properties, perovskite, thermal analysis

Introduction

From an ecological point of view pigments containing toxic elements are banned. These strict ecological aspects affected many industrial branches. Therefore, a search of new non-toxic materials with the same or better properties which have these banned compounds is by a subject of research of many workplaces. Nowadays, the large group of special inorganic pigments is unusable and especially the anticorrosive pigments based on lead or chromates belong to this group too. Perovskites containing like these cations which have been an ability to create alkaline anticorrosive pigments, can be once from possible compensations [1]. Therefore, perovskites containing Ba^{2+} , Ca^{2+} and Sr^{2+} are by subject of our research.

The preparation of perovskites compounds as ceramic materials with excellent electric and magnetic properties for utilization with using calcination on lower temperature in the first step and following sintering on higher temperature must be used [2].

Ceramic materials based on perovskite structure are known for long time. Perovskite compounds have a generally chemical formula ABX_3 and they are derived from calcium titanate, a naturally occurring mineral CaTiO_3 . It covers a wide range of colours from black, brown, gray, orange to yellow. Crystals of perovskite appear as cubes, but this is deceiving. Perovskite is actually pseudocubic. It is really orthorhombic in symmetry, but its structure is very close to

isometric [3]. In ABX_3 structure ion A has a larger size than ion B, and most of the metallic ions in the periodic table can be built in lattice of perovskites [4, 5]. The majority of the perovskite compounds are oxides or fluorides, but other forms as halides, sulphides, hydrides, cyanides, oxyfluorides and oxynitrides are also known [4, 6, 7].

Perovskites are very well known compounds and they can be synthesized with using different methods of preparation, particularly fine powder BaTiO_3 can be prepared by traditional solid state reaction method [8–11], co-precipitation method [12], hydrothermal method [13, 14], a solvothermal method [15], alkoxide hydrolysis [16], metal-organic processing [17], the Pechini process [18], etc. Mechanism of formation of this compound was also studied in detail [8, 19].

Perovskites as the ceramic materials have excellent electric and magnetic properties and thanks to their properties they find widely using in an industry. These materials can accommodate a large content of oxygen vacancies; therefore, some perovskites are good oxygen ionic conductors. The small B-site in the perovskite formula ABO_3 allows first row transition elements to be introduced in the lattice. These elements exhibit multivalence under different conditions, which may be the source of electric conductivity. Good ionic and mixed conductivity is found in several perovskite oxides [20]. For example barium titanate based on the wide variety of applications for which it is used, such as capacitors,

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positive temperature coefficient thermistors, piezoelectric devices, optoelectronic elements [2].

Basic properties of the pigments are necessary to know for next pigment utilization. They can be characterized by their chemical composition and by physical properties. The most commonly measured pigment properties are elementary analysis, impurity content, crystal structure, particle size distribution, density, surface area and optical properties [21]. BaTiO₃, SrTiO₃ and CaTiO₃ with perovskite structure were prepared in this work. The main aim was focused on influence of calcination temperature on colour properties of selected compounds. Methods of thermal analysis and X-ray diffraction analysis were used for these studies.

Experimental

The studied perovskites were prepared by solid state reaction [8, 11]. As starting materials for preparation of the tested compounds were used BaCO₃, SrCO₃, CaCO₃ and TiO₂ (anatase). The purity of all raw materials was in range of 96–99%. The starting mixtures were homogenized in an agate mortar in stoichiometric ratio. The mixtures were calcinated in corundum crucibles in an electric resistance furnace with the increase of the temperature 10°C min⁻¹. The samples were calcinated in temperatures 1000, 1100 and 1200°C for the duration 3 h. The calcinated samples were washed by hot distilled water, filtered and dried.

The main aim was focused on the study of the influence of calcination temperature on the colour properties of tested compounds. The colour properties of powdered pigments and pigments applied into the transparent glaze P 07491 (Glazura, s.r.o, Roudnice nad Labem, Czech Republic) in mass ratio 10% were measured in the visible region of light (400–700 nm) with using ColourQuest (HunterLab, USA). The measurement conditions were following: illuminant D65 (6500 K), 10° complementary observed, geometry of measurements d/8°. The colour properties were described in terms of CIE *L*a*b** system (1976). The value *L** represents the lightness or darkness of the colour. In the CIE *L*a*b** system it is described by numbers zero (black) to hundred (white). In this system *L**=50 corresponds to the grey colour. The values *a** (the axis red-green) and *b** (the axis yellow-blue) indicate the colour hue.

The thermal analysis was used for characterization of thermal behaviour and formation of tested perovskites. Thermal analysis of raw materials was performed by STA 449C Jupiter (Netzsch, Germany). This apparatus allows the simultaneous registration of the thermoanalytical curves TG and

DTA. The starting raw materials were studied by thermal analysis in ceramic crucibles in air in temperature region 30–1200 (1400)°C. The increase of temperature was 10°C min⁻¹. α-Al₂O₃ was used as reference material [22].

The structures of tested powdered samples were studied by X-ray diffraction analysis with using the diffractometer D8 Advance (Bruker, GB), with CuKα radiation and scintillation detector (the range 2θ from 10 to 80°).

Results and discussion

The thermal analysis has been used for study of the synthesis of powdered materials. The thermoanalytical curves TG and DTA can provide information about pigment formation.

Figure 1 demonstrates the thermoanalytical curves TG and DTA for mixture containing SrCO₃ and TiO₂, these curves were monitored in temperature interval 30–1250°C. The three endothermic and one exothermic peaks are evident on DTA curve. The first endothermic peak with the minimum at 793°C rather is connected with the start of transformation or decomposition of the SrCO₃. The second one, which is endothermic with minimum 938°C, corresponds to the change of orthorhombic to hexagonal transformation of the SrCO₃ [23]. The third peak, which is exothermic with the maximum 1036°C, is connected with the formation of strontium titanate compound or another by-products following SrTiO₃ as the main product [24]. The last one, pointed to that is endothermic effect with minimum 1185°C agrees with the

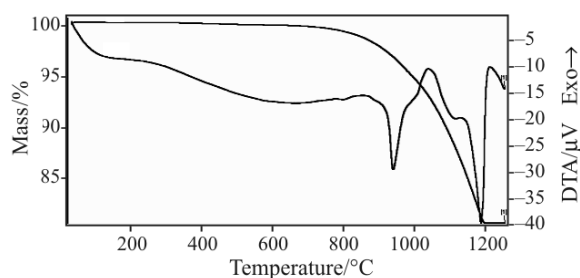


Fig. 1 DTA and TG curves of the mixture containing SrCO₃ and TiO₂ (sample mass 314.00 mg)

Table 1 Thermal decomposition of the reaction mixture containing SrCO₃ and TiO₂ (Fig. 1)

Temp. range/°C	Peak temp./°C	Total mass loss/%
700–1200	793	19.5
	938	
	1036	
	1185	

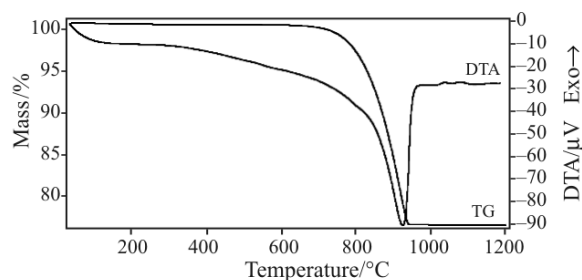


Fig. 2 DTA and TG curves of the mixture containing CaCO_3 and TiO_2 (sample mass 264.00 mg)

Table 2 Thermal decomposition of the reaction mixture containing CaCO_3 and TiO_2 (Fig. 2)

Temp. range/°C	Peak temp./°C	Total mass loss/%
650–940	924	23.47
	1038	
950–1200	1077	

total decomposition of the SrCO_3 . Total mass loss (Table 1), which is shown on TG curve of this TG-DTA record, is 19.5% and caused with decomposition of SrCO_3 .

The simultaneous TG-DTA analysis has been also used for starting mixture containing CaCO_3 and TiO_2 (Fig. 2). The temperature region of this measurement was from 30 to 1200°C. The DTA curve shows three peaks, the one endothermic and two exothermic peaks. The endothermic effect on DTA curve with minimum 924°C belongs to the decomposition of CaCO_3 [25]. The following two exothermic peaks with maximum 1038 and 1077°C are connected with formation of calcium titanate. Total mass loss in interval 700–940°C is 23.47%, it is corresponding with decomposition of CaCO_3 and it is written on TG curve of this simultaneous thermal record (Table 2).

Barium carbonate exists in three crystallographic structures: rhombohedral, hexagonal and cubic form. DTA and TG thermoanalytical determination was measured in interval of the temperatures 30–1400°C and the record of this analysis is shown in Fig. 3. The first two endothermic peaks with the minimum 643 and 672°C probably may correspond with change of anatase form of TiO_2 . Next endothermic peak with the minimum 815°C is pointed out transformation of BaCO_3 from rhombohedral to hexagonal form and the endothermic effect with the minimum 987°C belongs to transformation of BaTiO_3 from hexagonal to cubic form and the start of decomposition of BaCO_3 [26]. Two exothermic peaks with maximum 938 and 1036°C and one endothermic effect with the minimum 1090°C are connected with the formation of by-products

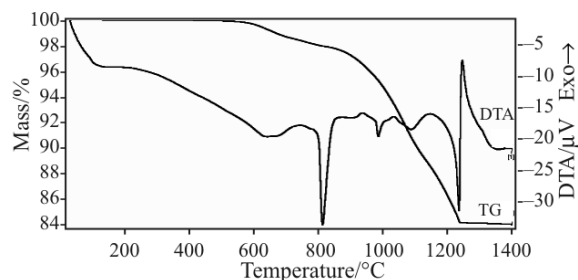


Fig. 3 DTA and TG curves of mixture containing BaCO_3 and TiO_2 (sample mass 360.90 mg)

Table 3 Thermal decomposition of the reaction mixture containing BaCO_3 and TiO_2 (Fig. 3)

Temp. range/°C	Peak temp./°C	Total mass loss/%
	643	16.06
550–850	672	
	815	
	938	
	987	
850–1250	1037	
	1090	
	1238	
	1248	

following formation of Ba_2TiO_4 and BaTiO_3 too [11, 19]. The last endothermic effect with minimum 1238°C signals finish of decomposition of BaCO_3 and the last exothermic peak with maximum 1248°C may correspond to formation only single-phase of BaTiO_3 [25]. The loss of the mass is recorded on TG curve, firstly mass loss is very sluggish, but in temperature region around 550–850°C mass loss is 2% and it probable corresponds with change of anatase. Between 850–1250°C mass change is observed (mass loss 14.06%) and this change is related with total decomposition of BaCO_3 . The total mass loss is 16.06% (Table 3).

The goal of this work was to study the influence of increase of calcination temperature on colour properties of tested perovskites. From this reason the colour properties of powdered compounds and compounds applied into ceramic glaze were determined. In colour space CIE $L^*a^*b^*$ coordinate L^* corresponds to brightness and coordinates a^* and b^* correspond to a colour hue, a^* changes from green to red and b^* from blue to yellow.

Colour properties of powdered compounds are described in Table 4. This table shows that all tested powders have light hues. BaTiO_3 calcined at 1000°C has the white colour with the very little part of green hue (coordinate a^* is in negative field of colour

space). But value of a^* increases with the growing temperature and it slowly shifted to the red field of colour space. Coordinate b^* increases with the temperature too and it obtains more yellow hues. The change of colour of BaTiO₃ is shifted from the white to the beige. All powdered samples of SrTiO₃ have the white colour. This colour with the increase of calcination temperature changed but these changes were very small. From Table 4 it follows that coordinates a^* and b^* of tested SrTiO₃ increase and the colour obtains more the red and the yellow hue. The colour result of SrTiO₃ calcined at 1200°C is the creamy. The colour change of CaTiO₃ powders in dependence on temperature was evident. The sample calcined at 1000°C is the white, but the increase of calcination temperature has effect on colour hue.

Table 4 The colour properties of the powdered compounds

Sample	Temp. of calcination/°C	L^*	a^*	b^*
BaTiO ₃	1000	91.15	-0.82	5.65
	1100	87.98	-0.03	7.44
	1200	86.78	0.94	9.48
SrTiO ₃	1000	89.69	1.11	3.54
	1100	88.54	1.59	3.83
	1200	89.31	1.95	4.77
CaTiO ₃	1000	81.60	2.08	7.54
	1100	78.00	5.87	6.30
	1200	80.90	5.46	6.82

Table 5 The colour properties of the samples applied into glaze P 07491

Sample	Temp. of calcination/°C	L^*	a^*	b^*
BaTiO ₃	1000	78.24	3.11	20.86
	1100	78.73	2.70	20.41
	1200	79.50	2.37	22.18
SrTiO ₃	1000	81.05	2.95	19.07
	1100	77.79	3.05	18.00
	1200	79.75	3.18	18.50
CaTiO ₃	1000	84.86	1.38	12.17
	1100	81.00	2.46	19.73
	1200	83.82	1.70	11.39

Table 6 The phase composition of tested perovskites calcinated at different temperatures

Sample	Calcination temperature/°C		
	1000	1100	1200
CaTiO ₃	TiO ₂ , CaTiO ₃ , Ca(OH) ₂	CaTiO ₃ , TiO ₂	CaTiO ₃ , TiO ₂
SrTiO ₃	TiO ₂ , Sr ₂ TiO ₄ , SrTiO ₃ , SrCO ₃	SrTiO ₃ , Sr ₂ TiO ₄ , TiO ₂ , SrO, SrCO ₃	SrTiO ₃ , TiO ₂
BaTiO ₃	BaTiO ₃ , Ba ₄ Ti ₁₃ O ₃₀ , BaCO ₃ , TiO ₂	Ba ₄ Ti ₁₃ O ₃₀ , BaTiO ₃	BaTiO ₃ , Ba ₂ TiO ₄

Table 4 shows that colour coordinate a^* with the temperature increases and hue shifts into red field of the colour space. Coordinate b^* is decreased, but this change is very small. The colour of this compound was beige.

Tiles with the applied compounds can be characterized as follows, the colours of tiles are not interesting and they move in different light beige hues and surface of tiles is without crack. These compounds have lower hiding power. Colour properties of perovskites applied into transparent ceramic glaze are given into Table 5. It is evident that changes in coordinates a^* and b^* are very small too. In case of BaTiO₃ coordinate a^* decreases with the increase calcination temperature, but the same coordinate increases for the SrTiO₃. Colour properties of CaTiO₃ are without evident trend.

The structures of tested powdered compounds were studied by X-ray diffraction analysis. Table 6 shows the phase composition of perovskites calcined at different temperatures. It is evident that in this case one-phase compound has been not prepared. X-ray patterns obtained for all samples calcined at 1000°C contain next to perovskites non-reacted starting raw materials and by-products corresponding to formation of SrTiO₃ and BaTiO₃, respectively, these results agree with the results of thermal analysis because the increasing of calcination temperature makes a change of composition. Fractions of raw materials and by-products are decreased and the intensive diffraction lines are obtained. However, the higher calcining temperature (about 1200°C) or longer time of calcination is necessary for preparation of single-phase substances.

Conclusions

The preparation of CaTiO₃, BaTiO₃ and SrTiO₃ was followed in this study. The temperature of the perovskite formation and their thermal stability were determined by the thermoanalytical measurements. The tested compounds have a good thermal stability in temperature region 1000–1200°C. The main goal was to study the influence the calcining temperature on colour properties. All samples have light colour hues and it was evident that calcination temperature

has the influence on the colour properties of perovskite compounds, but it is very small in tested temperature region. Therefore it was suitable to study this influence for higher temperatures. The results of X-ray diffraction analysis confirmed that higher calcining temperature (1200°C) is necessary for preparation of one-phase perovskite compound.

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