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Synthesis of Co-doped ceramics in the system $CaO{\cdot}xCoO{\cdot}1–xZnO{\cdot}2SiO_2$

Синтез на Co-дотирана керамика в системата $CaO{\cdot}xCoO{\cdot}1–xZnO{\cdot}2SiO_2$

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Introduction

Ceramic pigments are inorganic materials containing transition chromophore elements that are added to produce the corresponding color of the bulk ceramics. The pigments form a heterogeneous mixture with the matrix in which they are dispersed, affecting the properties of the ceramics. In addition to coloring properties, ceramic pigments must be resistant to atmospheric and chemical influences, to high temperatures, to the action of silicate melts, and to prolonged exposure to light. Ceramic pigments must be insoluble in water, in organic solvents and binders, but dispersed therein, altering the optical characteristics of the materials.

Cobalt-based pigments are widely used for coloration in blue glazes and bulk ceramics (Ozel et al., 2010; Mantovani et al., 2015). In fact, the color of Co compounds depends on the coordination of the ion in the crystal lattice of the host mineral (Thejusa et al., 2018). In our previous studies, we have proven the effect of CoO concentration as an oxide that gives a saturated blue color of synthesized willemite (Zn_2SiO_4) pigments (Ibreva et al., 2018).

In the present work, we report the synthesis of blue ceramics with composition $CaO{\cdot}0.2CoO{\cdot}0.8ZnO{\cdot}2SiO_2$, consisting of tridymite, cobalt-doped willemite and hardystonite.

Experimental details

Synthesis

The materials used for the synthesis are CaO, ZnO, CoO and $SiO_2.nH_2O$. The $SiO_2.nH_2O$ with particle size in the range 2–7 μm is much more reactive than conventionally used as a source of SiO_2 quartz sand. The content of SiO_2 (76.3%) and H_2O (23.7%) in $SiO_2.nH_2O$ was determined after calcination in a platinum crucible. Ceramics was synthesized via solid-state high temperature sintering. No mineralizer was used. The calculated quantities of materials for 100 g batch are weighed with a precision, then mixed and dry homogenized in planetary mill PULVERIZETE-6 (FRITCH). Synthesis was carried out in a laboratory muffle furnace in porcelain crucibles with a heating rate of 300–400 °C/h in air with isothermal retention of 1 hour at the final temperature. The resulting ceramics was sintered at 1100 °C. The compositions of the synthesized ceramic mixture is $CaO{\cdot}0.2CoO{\cdot}0.8ZnO{\cdot}2SiO_2$.

Characterization

The resulting blue ceramics was examined by powder X-ray diffraction (XRD) analysis, scanning electron microscopy with energy dispersive X-ray microanalysis (EDAX), infrared spectroscopy and spectrophotometric measurements.

Phase composition was determined using D2 Phaser–Bruker AXS Bragg-Brentano diffractometer operating at 30 kV and 10 mA with CuKα radiation, over a range of 3–70 2θ with a step size of 0.05 2θ and a counting time of 1 s/step.

FTIR spectra were collected using a Tensor 37 spectrometer (Bruker) with 4 cm^{-1} resolution after averaging 72 scans on standard KBr pallets in the spectral region 400–4000 cm^{-1} at room temperature.

Secondary electron (SE) images, backscattered electron (BS) images and EDAX analysis of the materials were carried out on JEOL 6390 equipped with INCA Oxford analyzer at acceleration voltage of 20 kV and beam current of 500 pA. The standardless quantification results were performed through automatic background subtraction, matrix correction, and normalization to 100% for all of the elements in the peak identification list.

The color of the ceramics was determined by Lovibont Tintometer RT100 Colour.

Results and discussion

X-ray diffraction (XRD) analysis

The powder XRD patterns of the ceramic sintered at 1100 °C is presented on Fig. 1a. The XRD patterns show well defined sharp peaks corresponding to hardystonite – $Ca_2ZnSi_2O_7$ (PDF #35-0745), willemite – Zn_2SiO_4 (PDF #46-1316) and tridymite – SiO_2 (PDF #42-1401) (Powder Diffraction File of the International Centre for Diffraction Data – ICDD). The peaks of corresponding phases are marked with small letters (Fig. 1a). Part of the SiO_2 has not reacted, forming crystalline orthorhombic SiO_2 – tridymite.

Due to close ionic radii (Zn^{2+} 0.60Å, Co^{2+} 0.58Å), Co for Zn substitution in hardystonite and willemite is common (Dondi et al., 2011; Ibreva et al., 2018).

SEM morphology and chemistry

Fig. 1b presents SEM micrograph in secondary electrons of dense hardystonite-willemite-tridymite ceramics. The EDAX analysis collected from ten points reveal dispersion of analyzed elements as follow: Si from 13.61 to 25.04 wt%, Ca from 2.24 to 25.87 wt%, Zn from 9.82 to 20.88 wt% and Co from 3.33 to 8.41 wt%. This points to uneven lateral phase and chemical distribution. Electron microprobe analysis indicate the presence of cobalt and calcium in all analyzed areas, but no correlation was found between the two elements. Since the XRD and IR analysis do not reveal the presence of cobalt oxide phase, we assume that cobalt enters the structure of both willemite and hardystonite.

FTIR analysis

FTIR spectrum (Fig. 1c) reveals strong and sharp absorption band at 1105, 1198, 790 cm^{-1} and shoulder near 474 cm^{-1} characteristic for crystalline SiO_2 (tridymite). Intensive absorption peaks at 971, 907, 838, 682, 618, 580, 482 and 460 cm^{-1} are indicative for hardystonite (Chukanov, Chervonnyi, 2016). According to previous assignment of vibrational modes of pyrosilicates (Sharma et al., 1988), the most intensive peaks due to stretching vibrations of Si_2O_7 atomic group are in the range 900–1000 cm^{-1}. The most intensive absorption of Co-doped willemite should appear in the range of stretching vibra-

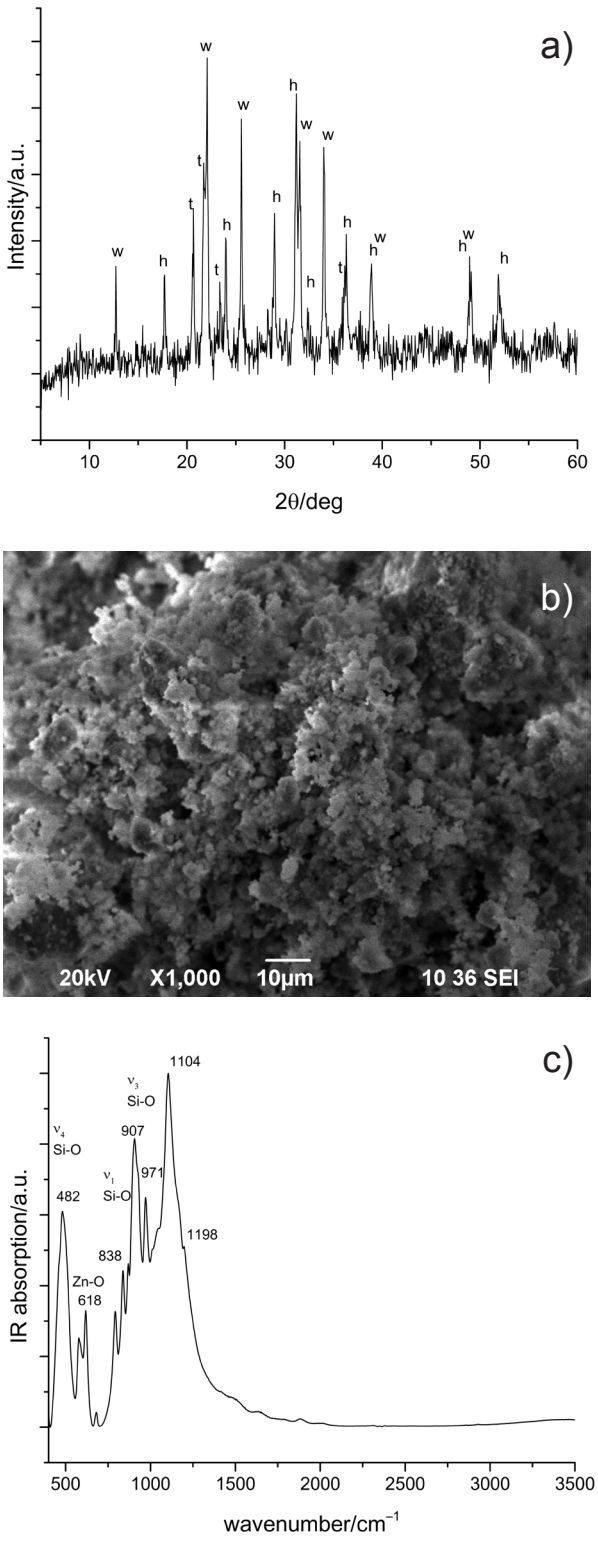

Fig. 1. *a*, powder XRD patterns of ceramics; *b*, SEM image of ceramics; *c*, FT infrared spectrum

tions of SiO_4 tetrahedral unit between 800–930 cm^{-1} (Ibreva et al., 2018). The peaks of Zn–O symmetric and antisymmetric stretching are near 580 and 614 cm^{-1}. The presence of these absorption peaks confirms that crystalline willemite and hardystonite are formed.

Color

The measured color coordinates are presented in the CIELab color space as defined by the International Commission on Illumination (CIE). The polyphase ceramics sintered at 1100 °C revealed much lower value of the blue color (b* = –26.1) and luminance (L* = 63.4) as compared to pure willemite ceramics with various concentration of Co, where the values of b* are in the range from –28.27 to –52.85 (Ibreva et al., 2018).

Conclusions

The polyphase ceramics with composition $CaO \cdot 0.2CoO \cdot 0.8ZnO \cdot 2SiO_2$ was synthesised via solid phase sintering method at 1100 °C. The resulting mineral phases are Co-doped hardystonite and willemite, as well as tridymite. The color coordinates of blue ceramics obtained are b* = –26.1; L* = 63.4 and a* = –3.5.

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