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STUDY OF DIOPSIDE CERAMIC PIGMENTS WITH RARE EARTH ELEMENTS

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Abstract: *Ceramics are synthesized via solid-state high temperature sintering at a temperature of 1000, 1100 and 1200°C in the system $CaO.xNd_2O_3.(1-x)MgO.2SiO_2$, where x = 0.1, 0.2, 0.3. The obtained ceramics were examined by powder X-ray diffraction analysis, electron scanning microscopy, infrared and UV-Vis spectroscopy. It has been found that under synthesis conditions a multiphase ceramics is obtained which contains in different ratio diopside, cristobalite, tridymite and traces of wollastonite. The colour of the ceramic changes to blue-greenish when vanadium is added to the system. The high concentration of vanadium leads to the formation of various polymorphic phases of SiO_2 and inhibits the formation of diopside. The efect of vanadium concentration and sintering temperature on phase composition and colour was studied.*

Keywords: *pigments, colour, ceramic, diopside*

INTRODUCTION

Diopside ($CaMgSi_2O_6$) is a widespread colorless mineral of pyroxene group with general formula M2M1T2O6. The chain structure of pyroxene offers much flexibility in the incorporation of various cations. Various ions can occupy different structural positions: in the M2 - Mg^{2+}, Fe^{2+}, Ca^{2+}, Li^{+}, Na^{+}, while in octahedral M1 position are Al^{3+}, Fe^{3+}, Fe^{2+}, Ti^{3+}, Cr^{3+}, V^{3+}, and others. In tetrahedral position (T) are Si and Al that form single chain parallel to c-axis. Incorporation of various elements in the crystal structure can led to change in physic-chemical properties of diopside and diopside-based ceramics. For example doping with transition d-elements was successfully applied for synthesis of diopside-based ceramic pigments (Pishch I., 1981), (Sedelnikova M. and V. Pogrebenkov, 2006), (Pogrebenkov V., M. Sedelnikova and V. Vereshchagin, 1999). The color of the natural and synthetic minerals is associated with the presence of transitional metals in the crystal structure, which have unfilled electron orbital. REE doped materials due to their 4f transitions are intensively studied in photonics and optoelectronic for various application - solar cells, fluorescent bio-imaging, solid state lighting, lasers, etc. Recently, REE doped silicates were proposed as low-toxic pigments possessing high reflectance in NIR spectral region (Jinga et al., 2018). The effect of REE (La, Ce, Pr and Nd) doping on the diopside glass-ceramics was studied via first principal investigation by Gao (Gao et al., 2019).

In natural diopside commonly contains low concentration of REE elements, most often bellow detection limit of the analytical method.

The aim of this study was to synthesize ceramics on the basis of stoichiometric diopside in the system $CaO.Nd_2O_3.MgO.2SiO_2$ at four different temperatures of sintering and to probe the ability to form Nd-doped diopside pigments in this system.

EXPERIMENTAL

Materials and method of synthesis

For the preparation of ceramic in the system $CaO.Nd_2O_3.MgO.2SiO_2$, the starting compositions are determined from the basic mineral diopside following the expression $CaO.xNd_2O_3.(1-x)MgO.2SiO_2$, where x = 0.1 and 0.2. Ceramic was synthesized via solid-state high temperature sintering at 900, 1000, 1100 and 1200°C.

Starting materials used for the synthesis are $CaCO_3$, Nd_2O_3, MgO and $SiO_2.nH_2O$ with particle size in the range of 2-7μm, which is much more reactive than conventionally used quartz sand as a source of SiO_2. 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 2 hour at the final temperature. The resulting powder mixtures were sintered at 900, 1000, 1100 and 1200°C in order to obtain Nd-containing ceramics.

The resulting powders were examined by powder X-ray diffraction (XRD) analysis, infrared spectroscopy (FT-IR) and the color was determined spectrophotometrically.

The phase composition was determined using X-ray diffractometer Empyrean, Malvern Panalytical operating at 40 kV and 30 mA with CuKα radiation.

FT-infrared spectra were collected using Tensor 37 spectrometer (Bruker) with 4 cm^{-1} resolution after averaging 128 scans on standard KBr pallets in the spectral region 400-4000 cm^{-1} at room temperature.

The colour of the resulting powders is determined by Lovibont Tintometer RT 100 Color and presented in the CIELab colour space.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis

X-ray diffraction patterns of the synthesized powder samples are shown on Fig. 1a, and Fig. 1b. The powder XRD data revealed that the presence of the rare earth element neodymium in the initial system with diopside composition completely changes the phase composition.

The identified mineral phases are presented quantitatively in Table 1.

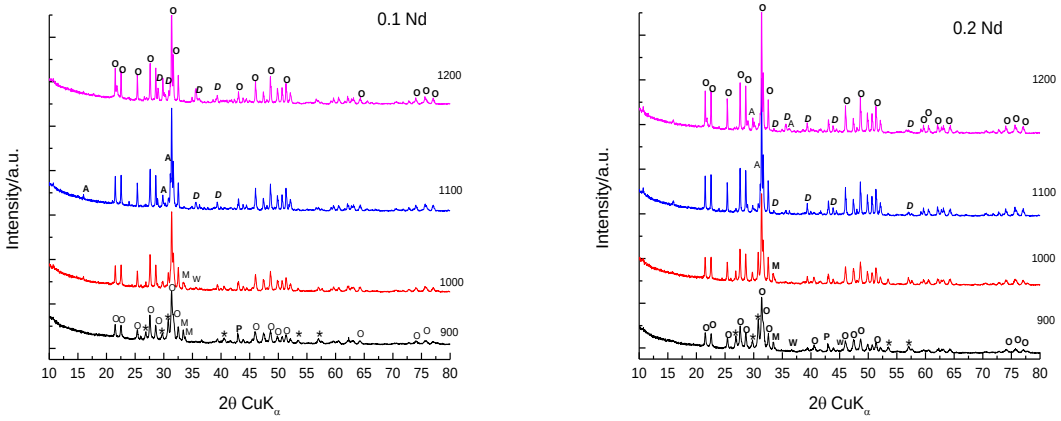

Fig. 1. XRD powder diffraction patterns of samples doped with 0.1 (a) and 0.2 (b) Nd sintered at 900, 1000 , 1100 and 1200 °C. O-oxyapatite $Ca_2Nd_8(SiO_4)_6O_2$; D – diopside; M-merwinite; W –wollastonite; A- äkermanite; P- periclase; *- Nd_2O_3

Table 1 Phase composition of samples doped with Nd sintered at 900, 1000 , 1100,1200 °C.

$CaO.0.1Nd_2O_3.0.9MgO.2SiO_2$								
T, °C	$Ca_2Nd_8(SiO_4)_6O_2$ Apatite-type	$Ca_3Mg(SiO_4)_2$ Merwinite	$CaMg(SiO_3)_2$ Diopside	Nd_2O_3	$CaSiO_3$ Wollasto-nite 2M/	$Ca_2MgSi_2O_7$ Äkermanite	MgO	SiO_2
900	58%	23%	-	10%	2-3%	-	7%	-
1000	73%	16%	-	6%	<1%	-	5%	-
1100	48%	-	32%	1%	<1%	17%	1%	-
1200	36%	-	38%	1%	8%	15%	-	<1%
$CaO.0.2Nd_2O_3.0.8MgO.2SiO_2$								
900	63%	17%	-	16%	2%	-	3%	-
1000	71%	16%	-	10%	<1%	-	3%	-
1100	63%	-	20%	2%	<1%	14%	1%	-
1200	52%	-	22%	1%	8%	15%	-	<1%

As can be seen from Table 1 and Figure 1, the predominant phase that is formed is the rare earth silicate with apatite-type of crystal structure $Ca_2Nd_8(SiO_4)_6O_2$ - Nd oxyapatite (dicalcium octaneodymium hexa orthosilicate dioxide). Nd silicate predominates in almost all studied samples, obviously inhibiting the formation of diopside. At low temperature it forms together with merwinite, while at 1100°C diopside begins to form. Only at low concentrations of neodymium (Nd 0.1) and at high temperatures (1200°C) diopside is formed in a competitive amount with $Ca_2Nd_8(SiO_4)_6O_2$. Together with diopside at 1100 and 1200°C äkermanite and wollastonite are formed. The excess of neodymium is separated in all samples as Nd_2O_3 phase, the amount of which decreases with increasing temperature. It can be assumed that the addition of neodymium in the system does not favor the formation of diopside based ceramics.

Infrared spectra (FT-IR)

The infrared spectra of studied poly-phased ceramics reveal broad and overlapping bands in the range of Si-O bond vibrations, as all established silicate phases have the most intense absorption in the range of 800-1100 cm^{-1} (Chukanov, 2014). The intensive absorption peaks at 920 and 530 cm^{-1} are probably due to $Ca_2Nd_8(SiO_4)_6O_2$, according to (5 Ning et al. 2019). At 1100 and 1200°C, the increase of the absorption at 1072, 970 and 880 cm^{-1} is probably due to the formation of diopside (Omori, 1971).

Color Measurement

Color is one of the most important indicators of the pigment quality. The color of the initial Nd_2O_3 used as a source for Nd in the system is pale grey-bluish. The color of the synthesized poly-phased ceramics is pale violet. The results obtained for color coordinates are shown in Table 2.

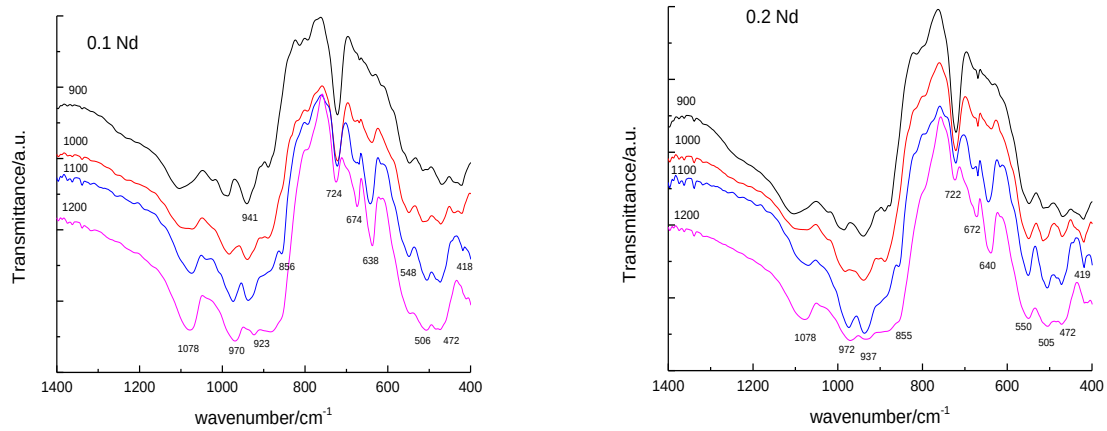

Fig. 2. FT-IR spectra of Nd-doped ceramics sintered at 900, 1000 , 1100 and 1200 °C:
a) $CaO.0.1Nd_2O_3.0.9MgO.2SiO_2$; b) $CaO.0.2Nd_2O_3.0.8MgO.2SiO_2$

Table 2. Results obtained for colour coordinates of the pigments

№	Composition	T°C	L*	a *	b *
1	$CaO.0,1Nd_2O_3.0,9MgO.2SiO_2$	900°C	95,3	-1,6	-4,3
2		1000°C	94,8	-0,5	-4,7
3		1100°C	93.8	0,4	-5,5
4		1200°C	93,4	1,3	-7,10

5	$CaO.0,2Nd_2O_3.0,8MgO.2SiO_2$	900°C	94,3	-1,5	-4,5
6		1000°C	94,1	-0,8	-4.9
7		1100°C	93,4	0,5	-5,4
8		1200°C	91,9	1,2	-7,4

A slight decrease of L* parameter is observed with increase of temperature and change of phase composition. This may be an indirect indication that color saturation is associated with diopside formation. The values of (-b*) is greatest in samples heated at 1200°C where the amount of diopside is highest.

CONCLUSIONS

Ceramics in the system $CaO.Nd_2O_3.MgO.2SiO_2$ were synthesized via solid-state high temperature sintering at 900, 1000, 1100 and 1200°C. The phase composition and its change depending on the sintering temperature are determined. It was found that in all studied samples a multiphase ceramics is formed as the predominant phase is $Ca_2Nd_8(SiO_4)_6O_2$ - Nd silicate with apatite-type of crystal structure. Diopside did not begin to form until 1100 and 1200°C. It can be summarized that the addition of neodymium to the initial system with a stoichiometric composition of diopside does not favor the formation of diopside-based ceramics.

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