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SYNTHESIS AND PHASE COMPOSITION OF Mn- AUGITE CERAMIC PIGMENTS

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Abstract: *Ceramics with initial composition corresponding to augite (Ca,Na)(Mg,Mn)(Si,Al)$_2O_6$ were synthesized in the system CaO–Na$_2$O–MnO–MgO–Al$_2$O$_3$–SiO$_2$ by high temperature solid-state sintering method. Three compositions with different magnesium to manganese ratios of 0.9:0.1; 0.8:0.2; and 0.7:0.3 mol %, respectively, were used, suggesting substitution at the M1 structural position. Ceramics prepared after sintering at 1000, 1100 and 1200 °C were examined by powder X-ray diffraction, infrared spectroscopy, scanning electron microscopy, and UV-Vis spectrophotometry. The resulting ceramics were found to consist of augite or Mn-augite with small amounts of bustamite as a minor phase.*

Key words*: augite, pigments, CIELab, color measurement*

INTRODUCTION

The general chemical formula for all pyroxenes is M2M1T$_2$O$_6$ (Morimoto N., 1988). The octahedral M1 structural position is occupied by six-fold coordinated cations (Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Ti^{4+}, V^{3+}, Co^{2+}, Zn^{2+}), M2-site is occupied by 6 to 8 coordinated cations (Ca^{2+}, Na^{+}, Fe^{2+}), and the tetrahedral position (T) is mainly occupied by Si^{4+} or by Si^{4+}, Al^{3+} and Fe^{3+} (Titorenkova, R et. Al., 2022,). Augite - (Ca, Na)(Mg, Fe, Al, Ti)(Si, Al)$_2$O$_6$ belong to the subgroup of Ca pyroxenes with wollastonite (Ca$_2$Si$_2$O$_6$) component content about 20–45%. It has limited substitution of Na^{+} for Ca^{2+} in M2, Al^{3+} for Mg^{2+} in M1, and Fe^{3+} and Al^{3+} for Si^{4+} in T positions (Mantovani, L, 2014). This makes the structure suitable for the synthesis of pyroxene ceramics with a more complex chemical composition. The aim of this study is to obtain Mn-augite colored ceramics by a high-temperature solid-state synthesis method and to determine the phase composition depending on the initial manganese concentration and the sintering temperature.

METHOD OF SYNTHESIS

The starting compositions determined on the basis of augite are:

A1) 0,9CaO.0,1Na$_2$O.0,9MgO.0,1MnO. 0,1Al$_2$O$_3$.0,9SiO$_2$

A2) 0,9CaO.0,1Na$_2$O.0,8MgO.0,2MnO. 0,1Al$_2$O$_3$.0,9SiO$_2$

A3) 0,9CaO.0,1Na$_2$O.0,7MgO.0,3MnO. 0,1Al$_2$O$_3$.0,9SiO$_2$

Starting materials used for the synthesis are CaCO$_3$, NaF, MgO, MnO, Al$_2$O$_3$ and SiO$_2$.nH$_2$O, calculated for 100 g batch. Powders were mixed, homogenized and sintered at three final temperatures. Solid-state synthesis was carried out in a laboratory muffle furnace in porcelain crucibles with a heating rate of 300-400°C/h and isothermal retention of 2 hour at the final temperatures of 1000, 1100 and 1200°C.

METHODS OF CHARACTERIZATION

XRD - Empyrean (MalvernPanalytical) powder X-ray diffractometer, equipped with a multichannel PIXcel^{3D} detector, using HDD Cu Kα (λ = 0.154060 nm) radiation, at 40 kV and 30 mA, in the range 3-100 °2θ and total time 35 minutes.

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

Scanning electron microscopy (SEM) images and microprobe elemental were performed with a JEOL JSM 6390 instrument equipped with an INCA Oxford EDS detector.

Color measurements using Lovibont Tintometer RT 100 Color are presented in the CIELab color space.

RESULTS AND DISCUSSION

XRD phase composition

The XRD patterns of the ceramics with various content of manganese sintered at different temperatures are presented on Figure 1.

The main phase that forms in all ceramic samples with different initial manganese concentration and temperature of sintering is augite. Bustamite ($CaMn^{2+}Si_2O_6$) is detected in all studied samples as a minor phase. Depending on the initial amount of manganese in the sample, different PDF cards from the crystallographic database of ICDD (The International Centre for Diffraction Data) were used for the mineral phase identification.

Phase analyzes of the crystallized components registered in the powder XRD patterns show that the ceramics with composition A1 contain major phase augite $Ca(Mg_{0.7}\ Al_{0.3})\ (Si_{1.7}Al_{0.3})O_6$ and traces of bustamite I $Ca(Mn,Ca)Si_2O_6$ (PDF No. 44-1455). The content of bustamite is insignificant and is bellow 1 wt.% in the sample obtained at a temperature of 1200°C. Powder XRD patterns of ceramics with composition A2 are similar, but the major phase is Mn-augite (PDF #78-1392) and traces of bustamite II $Ca_{0.8}Mn_{0.2}SiO_3$ (PDF #86-1607). The ceramics sintered at 1200°C is almost single phase Mn-augite. In the case of composition A3, the powder XRD patterns differ slightly. Mn-augite is dominant, but the content of bustamite II is higher at 1000°C, further increases slightly at 1100°C and finally at 1200°C bustamite II transforms to bustamite III $CaMnSi_2O_6$ (PDF #72-1446). The powder XRD results are clear indication of the degree of incorporation of manganese in the obtained phases with an increase of its concentration in the initial composition. The phase composition is summarized in Table 1.

Table 1. Phase composition of the ceramics sintered at different temperatures

Sample/Initial composition	T°C	Ceramic phase composition
Mn-augite 1 0,9CaO.0,1Na_2O.0,9MgO.0,1MnO. 0,1Al_2O_3.0,9SiO_2	1000	Augite, Bustamite I, cristobalite
0,9CaO.0,1Na_2O.0,9MgO.0,1MnO. 0,1Al_2O_3.0,9SiO_2	1100	Augite, Bustamite I
0,9CaO.0,1Na_2O.0,9MgO.0,1MnO. 0,1Al_2O_3.0,9SiO_2	1200	Augite, Bustamite I
Mn-augite 2 0,9CaO.0,1Na_2O.0,8MgO.0,2MnO. 0,1Al_2O_3.0,9SiO_2	1000	Mn-augite, Bustamite II, cristobalite
0,9CaO.0,1Na_2O.0,8MgO.0,2MnO. 0,1Al_2O_3.0,9SiO_2	1100	Mn-augite, Bustamite II
0,9CaO.0,1Na_2O.0,8MgO.0,2MnO. 0,1Al_2O_3.0,9SiO_2	1200	Mn-augite, Bustamite II
Mn-augite 3 0,9CaO.0,1Na_2O.0,7MgO.0,3MnO. 0,1Al_2O_3.0,9SiO_2	1000	Mn-augite, Bustamite II
0,9CaO.0,1Na_2O.0,7MgO.0,3MnO. 0,1Al_2O_3.0,9SiO_2	1100	Mn-augite, Bustamite II
0,9CaO.0,1Na_2O.0,7MgO.0,3MnO. 0,1Al_2O_3.0,9SiO_2	1200	Mn-augite, Bustamite III

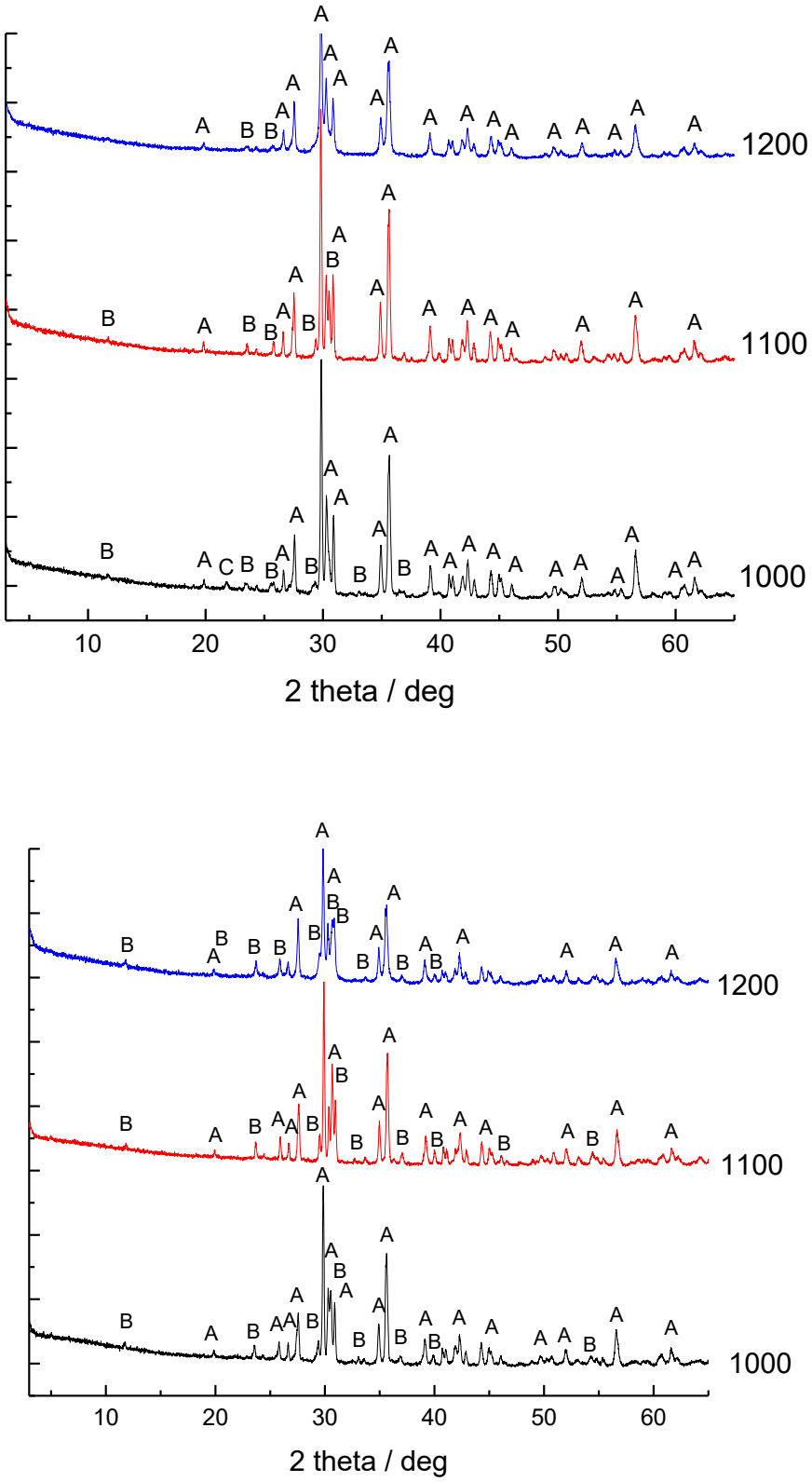

Fig. 1. Powder XRD patterns of ceramics with different Mn-content and temperature of sintering (1000, 1100 and 1200 °C): a) A1; b) A3.
Legend: A (augite); B (bustamite); C (cristobalite)

The formation of augite ceramics is also confirmed by infrared spectroscopy (Figure 2).

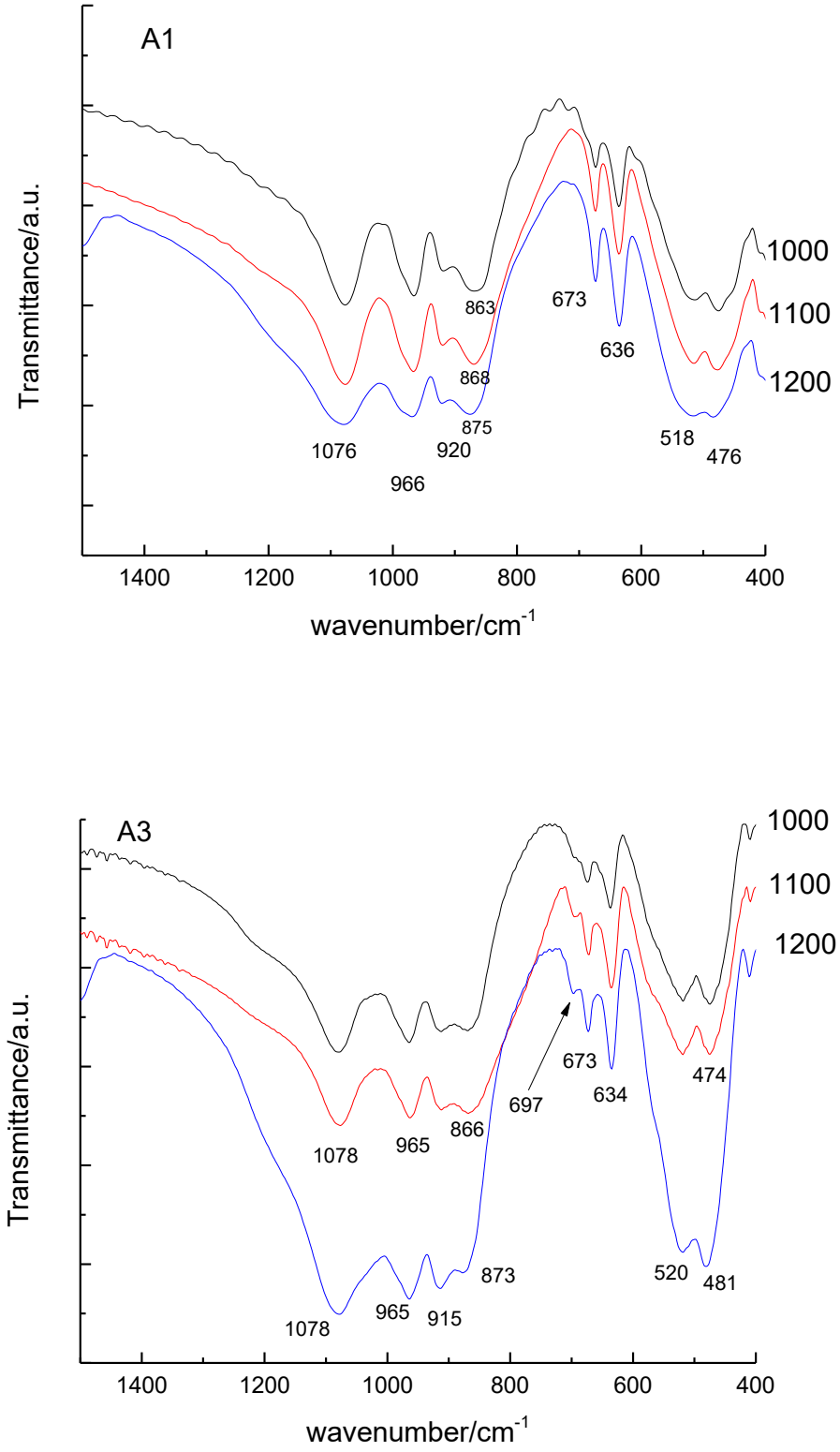

Fig. 2. Infrared spectra of ceramics with different Mn-content and temperature of sintering (1000, 1100 and 1200 °C): a) A1; b) A3.

The absorption maximum in the range 1080- 870 cm^{-1} indicate the presence of pyroxene [9] with characteristic peaks around 1076, 965 and 866 cm^{-1} which are due to Si-O stretching vibration in augite. The doublet at 673 and 634 cm^{-1} is also typical of pyroxene. An indication of the presence of bustamite is the peak at 697 cm^{-1} [10], which is visible in the spectrum of A3 (Fig.2 c), where the amount of this phase increases, confirming the XRD data.

Color

The color is presented according to the universal CIELab system by three coordinates L*, a* and b*. L* (Lightness) ranges from L* = 100 (diffuse white) to L*=0 (absolute black) in Table 2. The chromatic a* axis extends from green (-a*) to red (+a*), and b* axis extends from blue (-b*) to yellow (+b*). The results show that as the temperature of sintering increases from 1000 to 1200°C, the lightness increases and the color of the ceramics changes from beige to pale pink-purple with decrease of red color coordinates (a*).

Table 2. Results obtained from the measurement of the color coordinates

№	Composition	T, °C	Color	L*	a*	b*
1	0,9CaO.0,1Na_2O.0,9MgO.0,1MnO .0,1Al_2O_3.1,9SiO_2	1000		77,5	3,6	1,4
		1100		79,1	4,2	-1,4
		1200		86.0	1,5	-2,9
2	0,9CaO.0,1Na_2O.0,8MgO.0,2MnO .0,1Al_2O_3.1,9SiO_2	1000		68,1	2,9	2,9
		1100		68,9	3,4	0,7
		1200		87,7	0,8	0,4
3	0,9CaO.0,1Na_2O.0,7MgO.0,3MnO .0,1Al_2O_3.1,9SiO_2	1000		59,8	3,6	2,9
		1100		62,1	4,5	0,8
		1200		87,9	1,3	0,8

CONCLUSIONS

Pyroxene ceramics with addition of manganese in the range of 0.1-0.3 mol% were successfully synthesized by high-temperature solid-state sintering in the range 1000-1200 °C. The results reveal formation of augite or Mn- augite as a major crystalline phase and bustamite as a minor phase.

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