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AUGITE-BASED CERAMICS OBTAINED BY SOLID-STATE SINTERING OF LOESS

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ABSTRACT

Loess from the Danubian Plain (Bulgaria) was used as the raw material for the solid-state synthesis of ceramics. The mineral phase composition of the loess fraction used was determined by powder X-ray phase analysis, and the chemical composition by X-ray fluorescence analysis. The semi-quantitatively determined mineral phases are quartz, plagioclase, K-feldspar, mica, carbonates (calcite and dolomite), chlorite and amphibole. The major oxides of the chemical composition of loess fraction are (in wt. %): SiO_2 *- 53,61;* Al_2O_3 *- 12.57;* Fe_2O_3 *- 7.05;* P_2O_5 *- 0,23;* TiO_2 *- 1.37; CaO - 19.36; and MgO - 1.48.*

Experiments were performed with sintering of pure loess without additives, and with addition of MgO and Na_2O *in order to obtain a composition corresponding to that of the pyroxene augite -* $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$*. Ceramics were obtained at three temperatures: 1000, 1100 and 1200°C. The phase composition, spectral characteristics and colour coordinates of the obtained ceramics were determined. The results show that when magnesium and sodium are added to the loess raw material, the ceramics obtained after sintering at 1100 and 1200°C have a predominant content of augite and have a yellow-beige colour.*

Keywords: loess, ceramics, pyroxene, augite.

INTRODUCTION

Ceramic pigments based on diopside pyroxene matrices have been recently synthesized by solid-state method using pure chemical reagents [1, 2]. The search for cheaper materials, as well as the utilization of waste, require the use of other sources suitable as raw materials for the synthesis of such ceramics. When raw materials with complex composition are used, it is difficult to control the phase composition of the resulting final ceramic. For this reason, we chose as the main target phase augite, which can isomorphically incorporate a number of elements into its structure.

Augite ($(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$) is monoclinic, calcium deficient pyroxene with respect to diopside ($CaMgSi_2O_6$). The crystal structure of augite is flexible and allows isomorphic substitution in all crystallographic positions M1, M2 and T [3, 4].

The major elements that enter the structure of augite, besides calcium, magnesium, and silicon, are sodium, aluminium, iron, titanium [5]. This makes the structure suitable for the synthesis of pyroxene ceramics from raw materials with a more complex chemical composition, which contain iron, sodium, aluminium and other components. The expectation is that the appropriate elements can be isomorphically incorporated into the augite structure and thus prevent the formation of multiphase ceramics.

We aim to use a raw material with a higher silica content compared to marl to obtain ceramics with a predominant pyroxene content. The study of loess from Bulgaria shows that the content of the main oxides is in appropriate amounts, which correspond to their content in augite, except for magnesium. Therefore, we assessed that the chemical composition of loess is suitable for the purpose of synthesizing ceramics containing augite.

Loess is a sediment that is formed by the accumulation of wind-blown dust original material. Composed largely of silt-size grains that are loosely cemented by calcium carbonate. Loess soils cover a significant amount of the Earth's land surface, (~10 %). The dominant grain-size fraction within loess, falls within the range of 0.02 to 0.05 mm and encompasses grains of coarse and medium-grained silt. In Bulgaria, loess was deposited in an aeolian way during the Quaternary and covered in a mantle manner the existing Pliocene relief [6].

The formed loess horizons alternate with fossil soils (paleosoils), thus forming a common "loess complex". Sandy loess (with clay content less than 10 %) from the region of the Kozloduy was used as a source for ceramics. The most important advantages of loess are wide distribution, easy extraction, and suitable composition [7, 8].

The aim of the present study is to use loess as a row source for the solid-state synthesis of augite-based coloured ceramics.

EXPERIMENTAL

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 with a scanning rate of 0.013° for 80 s (total time 35 min). Pulse height distribution (PHD) optimization procedures have been applied to reduce the fluorescence-induced background and peak-to-background ratio.

Wavelength Dispersive X-ray Fluorescence Spectroscopy (WDXRF) was used to determine the chemical composition of the loess using Supermini 200 (Rigaku, Japan) spectrometer operating at 50 kV and 4.00 mA. The sample was crushed and pressed to obtain a tablet. The irradiated area of sample was 30 mm in diameter. The weight ratio of the amount of sample to the amount of glue (Acrawax C powder) was 5:1. A semi-quantitative method (SQX) was used to determine the elemental composition, without reference materials.

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

Raman spectroscopy - HR LabRam (Horiba) spectrometer (600 grooves/mm grating) coupled with an Olympus optical microscope and 50x objective in the range 100 - 4000 cm^{-1}. The 632.8 nm line of He-Ne laser was used for sample excitation. Origin 10 software package was used for spectral evaluation.

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

UV-Vis spectra were collected with spectrophotometer Cary 4000 (Bruker). The colour was determined by Lovibont Tintometer RT 100 Colour and presented in the CIELab colour space.

RESULTS AND DISCUSSION

Characterization of loess

The phase composition of loess was determined by powder XRD analysis (Fig. 1a.). The detected mineral phases are quartz, plagioclase, K-feldspar, mica, carbonates (calcite and dolomite), chlorite and amphibole. The infrared spectrum of loess (Fig. 1b.) confirms the presence of carbonate minerals with strong peaks at 878 and 1435 cm^{-1} arising from out-of-plane bending and non-symmetric stretching of carbonate groups, respectively. Also, intensive peaks in the range of O-H stretching around 3420 and 3620 cm^{-1} are characteristic of phyllosilicates (mica and chlorite) and amphibole.

The chemical composition of loess defined by WDXRF analysis is presented in Table 1. The major oxides CaO and SiO_2 are in amounts like their content in augite [5], but the magnesium content is much lower. To approach the composition of augite, it is necessary to add magnesium and sodium in the initial batch. Besides major oxides (Mg, Ca and Si oxides), loess contains aluminium, iron, titanium and potassium oxides, components that can enter the structure of augite in minor concentration.

Experiments

Experiments were performed with sintering of pure loess without additives, and with addition of MgO and Na_2O in order to obtain a composition corresponding

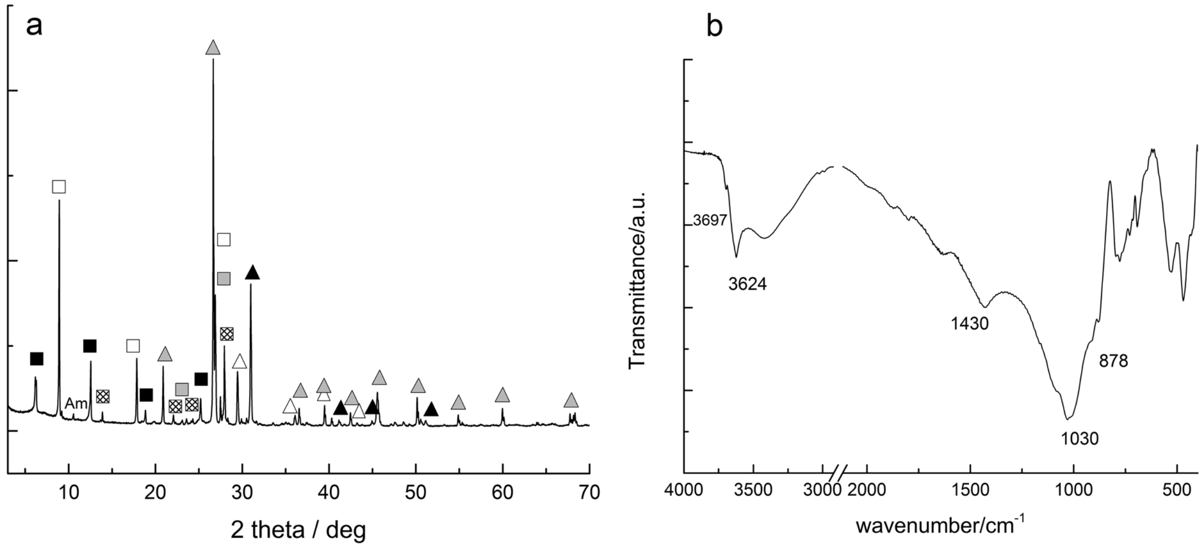

Fig. 1. (a) Powder XRD pattern of loess with legend: □ mica; ▲ quartz; ■ chlorite, ▩ plagioclase and K-feldspar, ▲ calcite, △ dolomite, Am - amphibole; (b) FT-IR spectrum of loess.

Table 1. Chemical composition of loess.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
Wt %	0.47	1.48	12.59	53.73	0.23	0.03	3.47	19.37	1.37	0.04	0.15	7.06

to that of the pyroxene augite - (Ca,Na)(Mg,Fe,Al,Ti)$(Si,Al)_2O_6$ [5]. The sample nomenclature and their composition are described in Table 2.

Calculated quantities of materials for 100 g batch are weighed, 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^{-1} in air with isothermal retention of 1 h at the final temperature. The resulting powder mixtures were sintered at 1000, 1100 and 1200°C for 2 h.

Ceramics characterization

The six ceramic samples (L1 and L2 at 1000, 1100 and 1200°C) obtained were examined using optical microscopy, scanning electron microscopy, powder XRD, infrared, Raman spectroscopy and colour measurements.

Morphological characteristics of loess (L0) and ceramics with composition L1 and L2, solid-state sintered at 1100 and 1200°C are presented in Fig. 2. It is seen from Fig. 2a that the most distributed grains of loess are bigger than 40 μm and falls in the range 0.1-0.005 mm in accordance with the reported data [7].

Table 2. Nomenclature and composition of the initial batches for the synthesis of ceramics.

№	Composition	Raw materials, g		
		Loess	NaF	MgO
L0	Loess raw			
L1	Loess sintered	15	–	–
L2	Loess + NaF + MgO	15	0.7	2.1

After sintering at high temperature, a pore ceramic was obtained with different size of pores and uneven distribution (Fig. 2c, d, e, f). The formation of such pores is due to the transformation of carbonate and phyllosilicates phases and releasing water, hydroxyl groups and mainly carbon oxides during the sintering process and cooling.

The phase mineral composition of the ceramics obtained at different temperatures is complex. It is presented in Fig. 3, and the full description of detected minerals is in Table 3.

The formation of augite was confirmed by electron probe microanalysis (EPMA). The calculated crystal chemical formulas of the studied augite are presented in

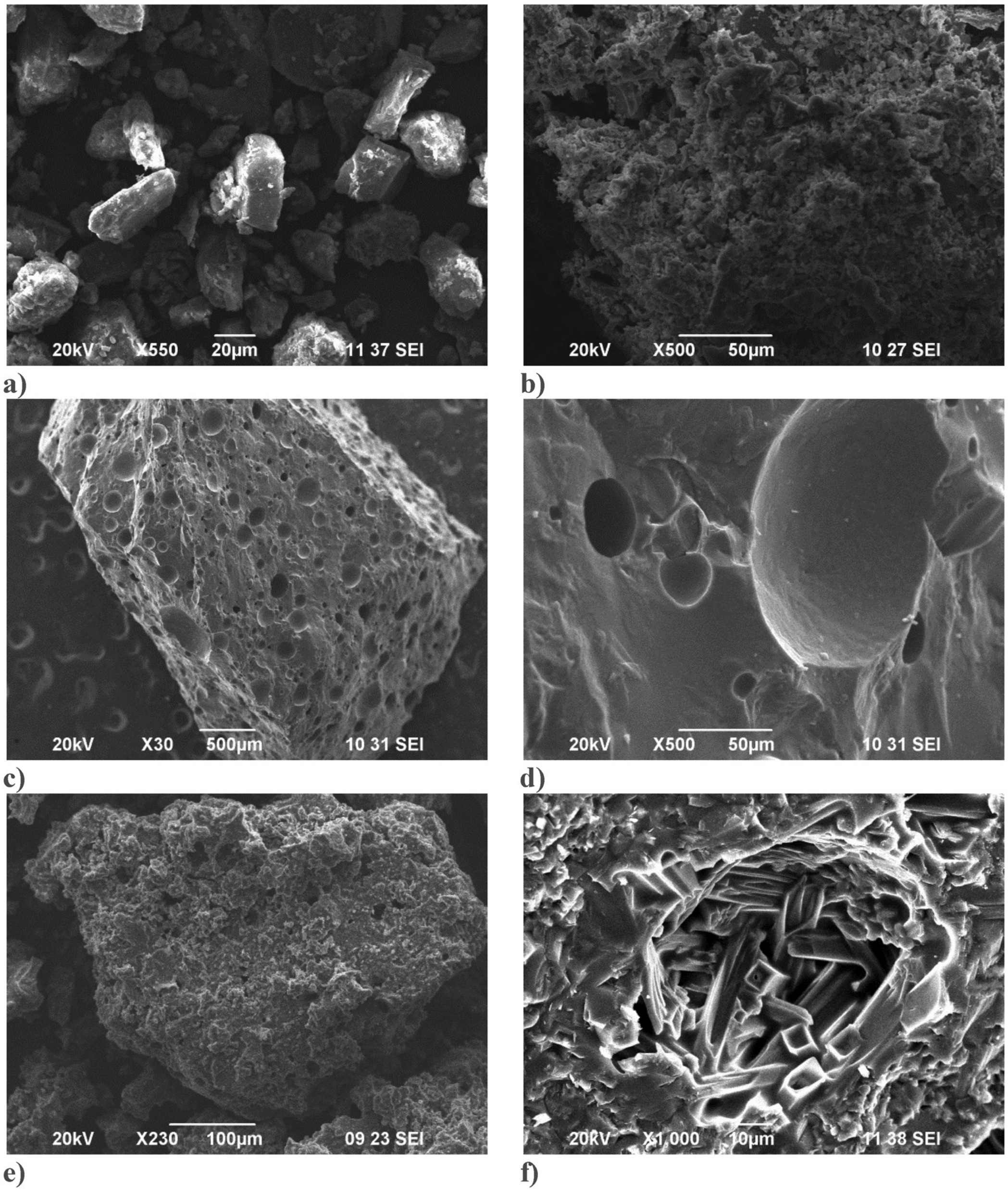

Fig. 2. SEM images of (a) the raw loess (L0) and (b) ceramics L1 sintered at 1100°C; (c) and (d) ceramics L1 sintered at 1200°C; (e) L2 sintered at 1100°C and (f) L2 at 1200°C.

Table 4. EPMA reveals only slight variation in the chemical composition of the studied augite grains (Table 4). T position in the pyroxene structure is almost fully occupied by Si and small amounts of Al are determined at this site. The composition is characterized by deficiency of calcium at M2 position, which is typical for the augites compared to other calcium clinopyroxenes. In some cases, M1 position is completely occupied by magnesium, while in others the amount of aluminium at this site is significant - up to 0.34 apfu.

When loess (L0) is heated, carbonates, mica and potassium feldspar are destroyed first. Plagioclase remains stable at 1100°C. The new phases formed in L1 are pyroxene-augite and gehlenite - $Ca_2Al[AlSiO_7]$. When heated above 900°C, pyroxene is formed by the reaction:

$2SiO_2 + CaMg(CO_3)_2$ (dolomite) $\rightarrow 2CO_2 + CaMgSi_2O_6$ (pyroxene).

In L2 ceramics, nepheline, augite, olivine (Mg_2SiO_4)

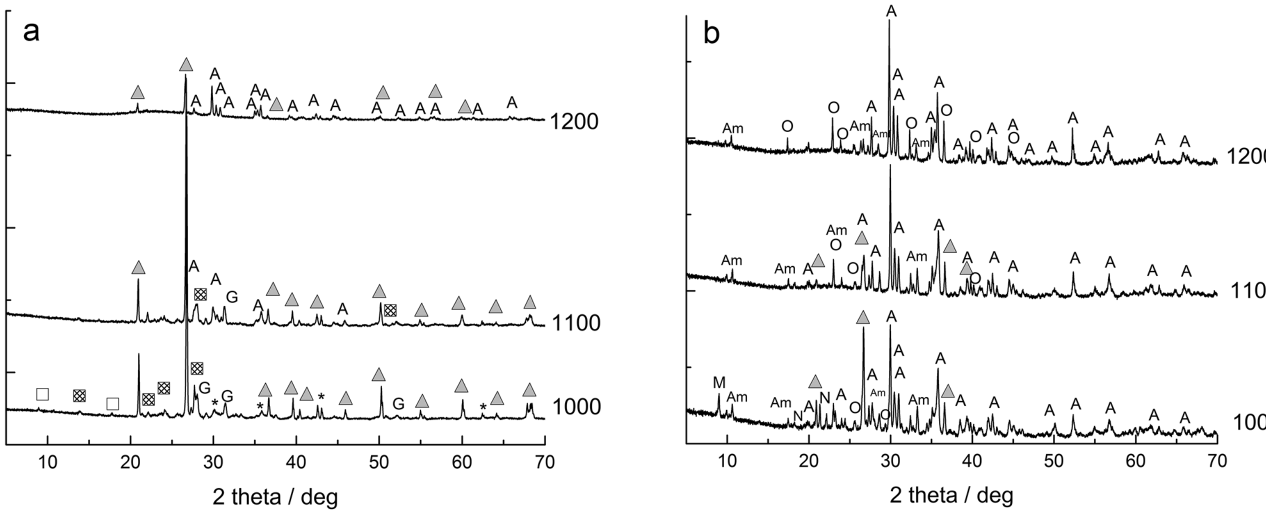

Fig. 3. XRD patterns of ceramics (a) L1 and (b) L2 sintered at 1000, 1100 and 1200°C (□ mica; ▨ plagioclase; G - gehlenite; Am - amphibole; ▲ quartz; A - augite; N - nepheline; O - olivine).

Table 3. Mineral phase composition.

Sample	Composition	Temperature Sintering	Mineral phases
L0			Quartz, Plagioclase, K-feldspar, mica, carbonates (calcite and dolomite), chlorite
L1	Loess	1000	Quartz, Mica, Plagioclase, Gehlenite
L1	Loess	1100	Quartz, Plagioclase, Augite, Gehlenite
L1	Loess	1200	Quartz, Augite, amorphous
L2	Loess + NaF + MgO	1000	Quartz, Nepheline, Augite, Amphibole, Olivine
L2	Loess + NaF + MgO	1100	Augite, Quartz, Amphibole, Olivine
L2	Loess + NaF + MgO	1200	Augite, Olivine, Amphibole, amorphous

and alkaline amphibole- $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}(OH)_2$ are the new-formed phases at 1000°C. At 1100 and 1200°C augite is prevailing phase. Only traces of olivine and amphibole are detected.

The infrared spectra of sintered loess (L1) (Fig. 4a) confirm the disappearance of the peaks of carbonate and hydroxyl atomic groups, due to the destruction of carbonates (calcite and dolomite) and phyllosilicates. Quartz is presented in almost all ceramic samples evident from the strong absorption near 1076 cm^{-1} and characteristic doublet at 794 and 774 cm^{-1} as well as strong absorption around 460 cm^{-1}. The change in phase composition with temperature in L1 is indicated by a shift in the position of the absorption maximum from 1009 cm^{-1} (L1 at 1000°C) characteristic of plagioclase to 1070 cm^{-1} (L1 at 1200°C) characteristic of augite and quartz. The peaks of the different phases overlap in the spectral range of Si-O stretching vibrations, and the intensity ratio can be an indication of the change in phase composition.

The strong peaks at 1068, 980 and 880 cm^{-1} visible in L2 are due to Si-O stretching vibration in augite. Peak at 519 cm^{-1} is characteristic for O-Mg-O bending vibrations in pyroxene [9]. Due to the different selection rules of the active vibrational modes, Raman spectroscopy was also applied to better distinguish the mineral phases and their relationships. Besides augite (668, 390, 328, 195 cm^{-1}) (Fig. 4) and quartz (460, 356, 200, 125 cm^{-1}), olivine (820 and 854 cm^{-1}) have been also confirmed in L2, sintered at 1100 and 1200°C [10].

Table 4. Chemical composition (EPMA, wt. %) and crystal chemical formulas of the separate augite grains (based on 6 oxygen atoms).

Samples Oxides	L2-1200-1	L2-1200-2	L2-1200-3	L2-1200-4	L2-1200-5	L0-1200-6
SiO_2	52.82	53.21	54.78	51.95	52.46	52.98
TiO_2	0.90	0.80	0.85	–	1.53	0.84
Al_2O_3	4.09	5.44	8.51	3.93	9.81	17.30
MgO	19.15	18.13	11.88	21.63	4.90	5.98
FeO_{tot}	4.72	4.97	5.15	7.65	10.06	5.26
CaO	16.45	14.99	14.98	12.67	14.72	12.87
Na_2O	1.83	2.15	2.6	0.84	1.35	2.37
K_2O	0	0.31	1.07	0.58	3.63	1.87
Σ	99.96	99.9	99.8	99.25	98.46	99.47
Atoms per formula unit (apfu)						
Si	1.91	1.92	1.97	1.90	1.97	1.89
Al^{IV}	0.09	0.08	0.03	0.10	0.03	0.11
Al^{VI}	0.08	0.15	0.33	0.07	0.40	0.62
Mg	1.03	0.97	0.64	1.18	0.27	0.32
Fe	0.14	0.15	0.15	0.23	0.32	0.16
Ti	0.02	0.02	0.03	0	0.04	0.02
Ca	0.64	0.58	0.58	0.50	0.59	0.49
Na	0.13	0.15	0.18	0.06	0.10	0.16
K	0	0.01	0.05	0.03	0.17	0.08

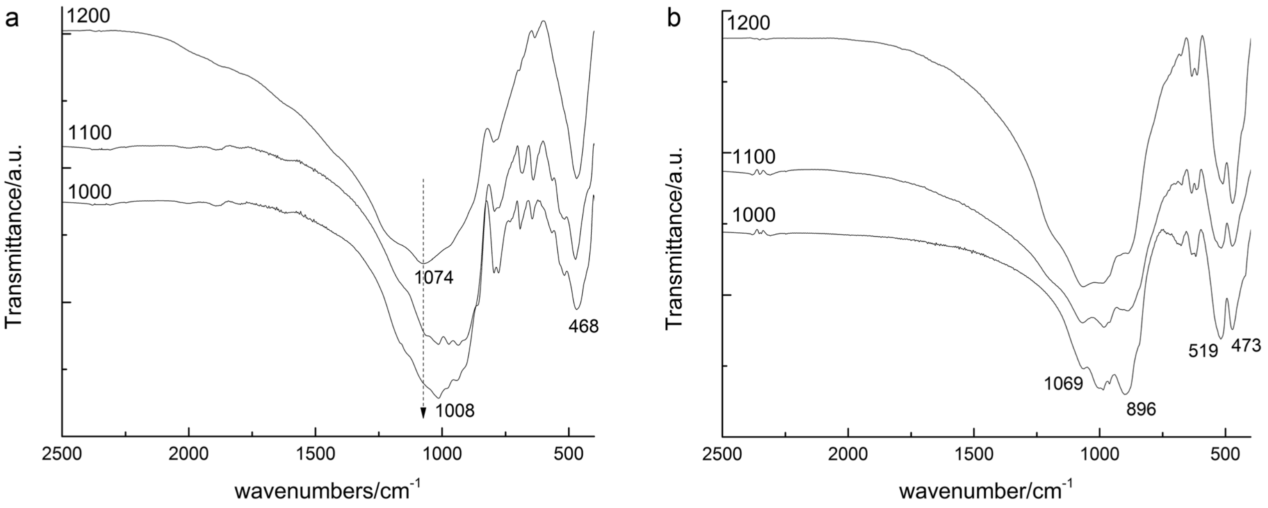

Fig. 4. FT-IR spectra of ceramics: (a) L1 and (b) L2 at 1000, 1100 and 1200°C.

Table 5. Results of colour coordinate measurements of pigments.

No	Composition	T°C	L*	a*	b*
L1	Loess	1000	65.8	11.3	23.2
		1100	63.1	7.0	21.6
		1200	54.1	–1.1	6.1
L2	Loess + NaF + MgO	1000	76.4	6.5	21.0
		1100	67.2	6.7	23.6
		1200	47.4	7.3	24.3

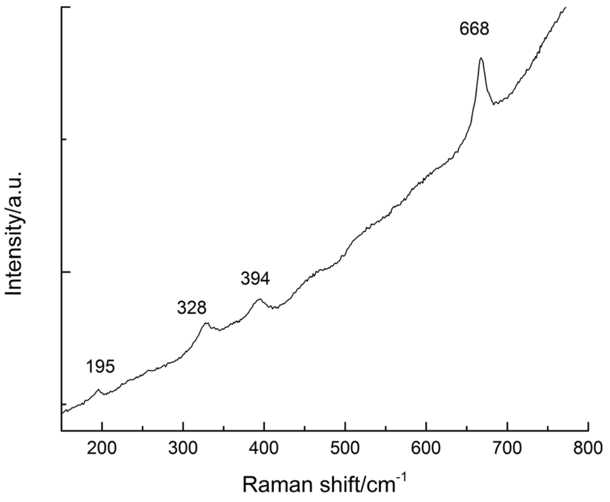

Fig. 5. Micro-Raman spectrum of augite from L2 at 1200°C.

Colour coordinates

The measured colour coordinates are presented in the CIELab colour space in Table 5 with three coordinates: lightness (L*), a* and b*. The chromatic axis a* extends from green (-a*) to red (+a*), and the chromatic b* axis extends from blue (-b*) to yellow (+b*). L* ranges from 100 (diffuse white) to 0 (absolute black).

Due to the complex composition, the interpretation of colour is not straightforward. However, it can be argued that as the sintering temperature increases for sample L2, the b* index increases, that is, the amount of yellow colour increases. Augite predominates in this sample with traces of the olivine and amphibole, which may also contribute to the colour. Interestingly, the trend for the colour coordinates of ceramics L1 and L2 is opposite. For L1, the green colour component increases with temperature. For L2, the yellow colour increases. We assume that the colour is due to the incorporation of various impurities in the augite structure in all crystallographic positions, but on the other hand to mixing with the colour of the other phases, in which also transition elements chromophores may be included.

CONCLUSIONS

Loess has been used as a source for obtaining pyroxene ceramics by the solid-state sintering method. When pure loess is sintered, a multiphase ceramic is formed, and at 1200°C the ceramic consists only of quartz and augite. When magnesium and sodium are added to the loess, the resulting yellowish-beige coloured ceramics after sintering at 1100 and 1200°C are porous and predominantly pyroxene-augite in composition.

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