OBTAINING OF GARNET CERAMIC MATERIALS BY UTILIZATION OF RICE HUSK ASH AS SILICA SOURCE

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ABSTRACT

The current research aims at the obtaining of new type pigments from the garnet mineral group by utilization of rice husk ash as silica source (RHA). At the beginning, the mixtures prepared from the starting raw materials are ground in a ball mill and then subjected to high temperature treatment. Green pigments were synthesized at two temperatures: 1000°C and 1100°C. Using the tintometer RT 100 Lovibond the colour characteristics were measured spectrophotometrically. The rice husk ash was investigated using scanning electron microscopy. The conducted hot-stage microscopic studies show that the pigments remain thermally stable when heated. The highest fire resistance - up to temperatures of 1380°C - 1400°C show the uvarovite pigments with main phase $3CaO.Cr_2O_3.3SiO_2$ or by a general formula $Ca_3Cr_2[SiO_4]_3$. They are suitable for inserting into ceramic glazes without danger of decomposition or reaction.

Keywords: ceramic pigments, SEM, colour determination, Hot-stage microscopy.

INTRODUCTION

Basically, pigments are substances that colour different materials. Unlike dyes, they consist of particles and are practically insoluble in the medium in which they are applied. Ceramic pigments are special solids, reduced to particles that can be colourful, black or white [1]. Aiming to get a full range of consistent ceramic colours, pigments are used with metallic oxides and salts. The colour of pigments is due to the presence of chromophores [2, 3]. There are several classifications of pigments. One of the most widely used is that of Turmanov. Turmanov identified the pigments according to their main crystal phase. Among the most important pigments are garnet pigments. Various minerals from the garnet group are found in the nature. In general, garnet have the following chemical formula $A_3B_2[SiO_4]_3$. The main representatives of the garnet group are: garnet pyrope, with chemical formula $Mg_3Al_2[SiO_4]_3$ - red in colour; almadine garnet - silicate of iron and aluminium, with the formula $Fe_3Al_2[SiO_4]_3$ - also red in colour, garnet grossular - it is a typical calcium aluminosilicate $Ca_3Al_2[SiO_4]_3$, with impurities of Fe^{3+}, Fe^{2+} - green in colour; garnet uvarovite - silicate of calcium and chromium ($Ca_3Cr_2[SiO_4]_3$) green in colour, etc. Because of their lasting and beautiful colours, many scientists are working on the synthesis of garnet pigments [4 - 7]. Pigments are of great importance to the silicate industry. The main colouring methods of ceramics are based on pigments [8].

The production of pigments from waste raw materials, in particular these from waste rice husk is of a particular interest. The authors of this paper have experience in the synthesis of garnet pigments from pure raw materials, but this paper examines the synthesis of garnet pigments, using ash from oxidized husk (RHA) [5].

EXPERIMENTAL

Methods

Colour Measurement

The colour determination of the pigments is determined spectrally by a tintometer of Lovibond Tintometer RT 100 Colour.

Scanning electron microscopy (SEM)

The SEM observations were carried out on an apparatus TESCAN, SEM/FIB LYRA I XMU at 30 kV accelerating voltage. The observations were accompanied by energy-dispersive Xray spectroscopy (EDS) carried out with a detector of Bruker.

Hot-stage microscopy (HSM)

High-temperature microscope ESS Misura HSM-1400 ODHT, model 1600/80, Italy (IFH-BAS) was used. The sample is heated to 1400^{o}C at a rate of 10^{o}C min^{-1}, and the graph reflects the changes that occur with it during heating.

Materials

A rice husk ash (RHA) obtained from oxidised at 660°C in air atmosphere rice husk was used as a source of silica. This rice husk (RH) contains organic matter (around 74.5 %), water and around 25.5 % inorganic oxides - 20 % SiO_2 and 5.5% mixture of the following oxides: Na_2O, K_2O, MnO_2, CaO, Fe_2O_3, MgO and Al_2O_3. These inorganic oxides, excluding SiO_2 play the role of mineralizer. Table 1 shows the composition and number of inorganic oxides in burnt rice husk ask.

The husk oxidation was carried out at the following temperatures: 500°C, 600°C, 650°C, 700°C, 850°C, 1000°C and 1200°C. The colour of the oxidized residue depends strongly on the burning temperature. Up to 500°C, the ash was almost black since the organic matter had not been burnt totally yet. At temperatures about 600-700°C, the initial rice husk sample turned into grey-white ash of varying intensity due to the presence of non-oxidized carbon in it while at higher temperature the product obtained was microcrystalline white ash with high content of SiO_2 due to full release of carbon.

Fig. 1 shows SEM images of air- burned rice husk at different magnifications. After the separation of the organic matter from the husk, mainly the inorganic mass forming the silicon-oxygen skeleton remains.

Table 1. Composition and number of inorganic oxides in RHA.

Component	Quantity, %
SiO_2	94.47
CaO	1.62
Fe_2O_3	1.36
MgO	1.08
Al_2O_3	0.98
MnO_2	0.49

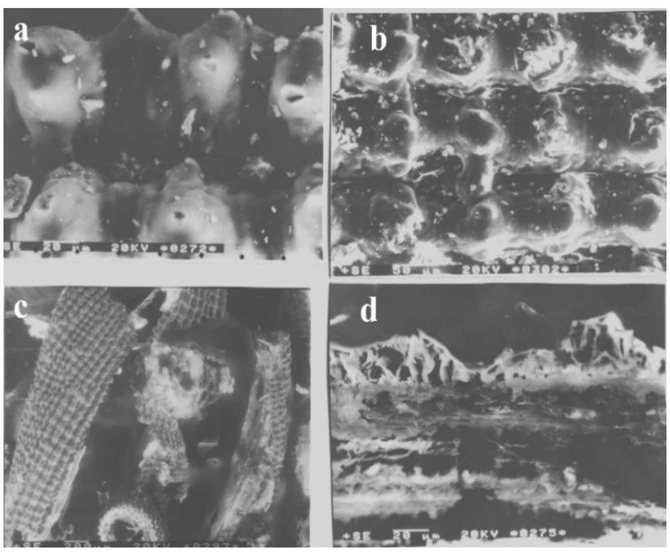

Fig. 1. SEM of oxidized rice husk.

Table 2. Compositions of synthesized garnet pigments and synthesis temperatures.

Sample No. / Garnet composition	Batch composition	Firing temperature
RH 1 $3CaO.Fe_2O_3.3SiO_2$ (andradite garnet pigments)	$CaCO_3$ Fe_2O_3 RHA	1000°C 1100°C
RH 3 $3CaO.V_2O_3.3SiO_2$ (vanadium garnet pigments)	$CaCO_3$ NH_4VO_3 RHA	1000°C 1100°C
RH 9 $3CaO.Cr_2O_3.3SiO_2$ (uvarovite garnet pigments)	$CaCO_3$ $K_2Cr_2O_7$ RHA	1000°C 1100°C

Fig. 2 shows the silicon-oxygen skeleton (Si-O-Si) of rice husk after burning the organics.

The blends' compositions are presented in Table 2. The synthesis temperatures are 1000°C and 1100°C for all three types of chromophores. As a starting raw material, CaO, Cr_2O_3, Fe_2O_3 and V_2O_3 have been used which were imported respectively through $CaCO_3$, $K_2Cr_2O_7$, Fe_2O_3 and NH_4VO_3. An amorphous RHA have been chosen as a silica (SiO_2) source. Firing was carried out with 2 hours isothermal soaking period at the final temperature.

The initial mixture was prepared by weighing the corresponding quantities of starting components. A planetary mill Pulverisette 6 (Fritsch, Germany) was used for homogenization and grinding of initial mixture. The high temperature final sintering were carry out at 1000 and 1100 for 2 h in air atmosphere in Naber furnace.

Fig. 3 presents photos of the starting composition as well as the synthesized pigments.

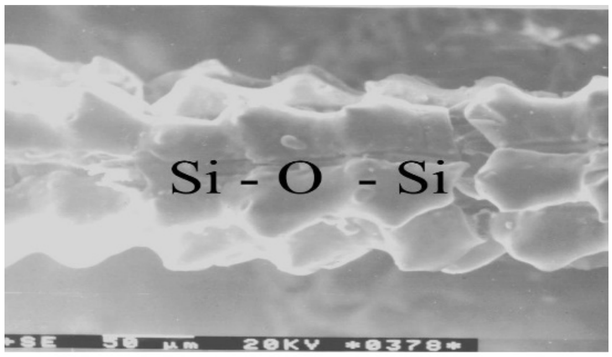

Fig. 2 The silicon-oxygen skeleton (Si-O-Si) of RHA.

Fig. 3. Initial mixtures (a) and synthesized pigments (b).

RESULTS AND DISCUSSION

Fig. 4 shows the technological scheme for the synthesis of the garnet pigments.

Conducted X-ray analysis proves the presence of a garnet phase. Fig. 5 shows X-ray analysis of andradite garnet pigments and Fig. 6 shows X-ray analysis of uvarovite garnet pigments.

Colour measurements

The most important properties of the pigments are their colour. It is known that the coloured materials absorb and transform light of certain wavelengths within the visible spectrum. Table 2 shows the results obtained from the measuring of the colours of the garnet pigments synthesized.

From the results from Table 2, the following is noticeable:

In the compositions with iron chromophore, the best results were obtained at RH1 (synthesized at 1000°C) -

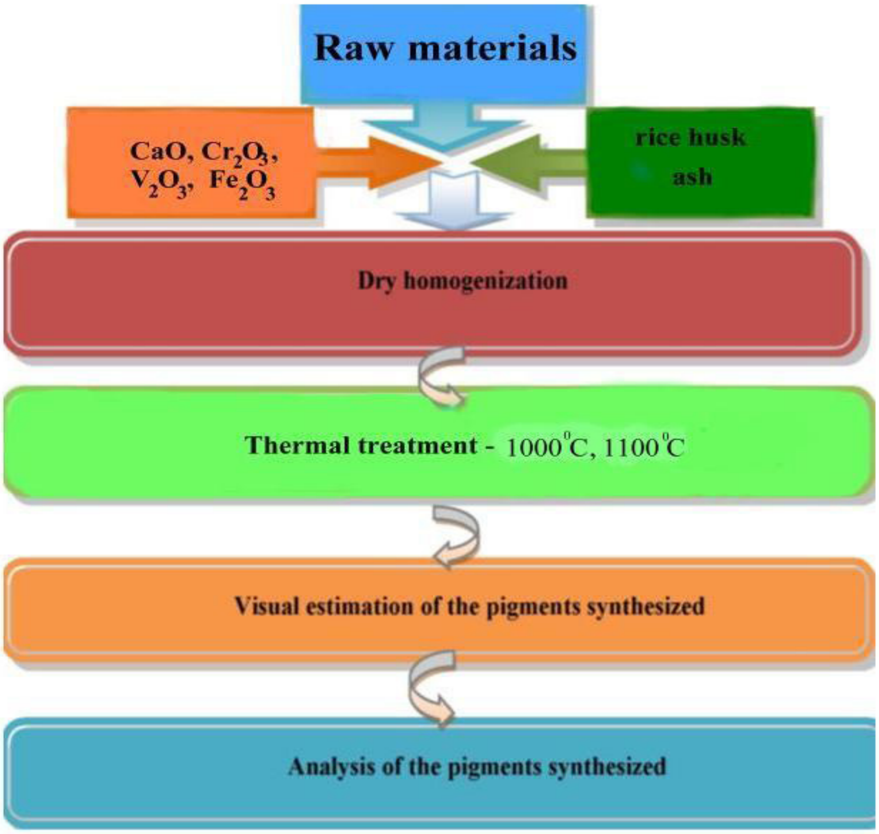

Fig. 4. Technological scheme for synthesis of garnet pigments, using RHA as silica source.

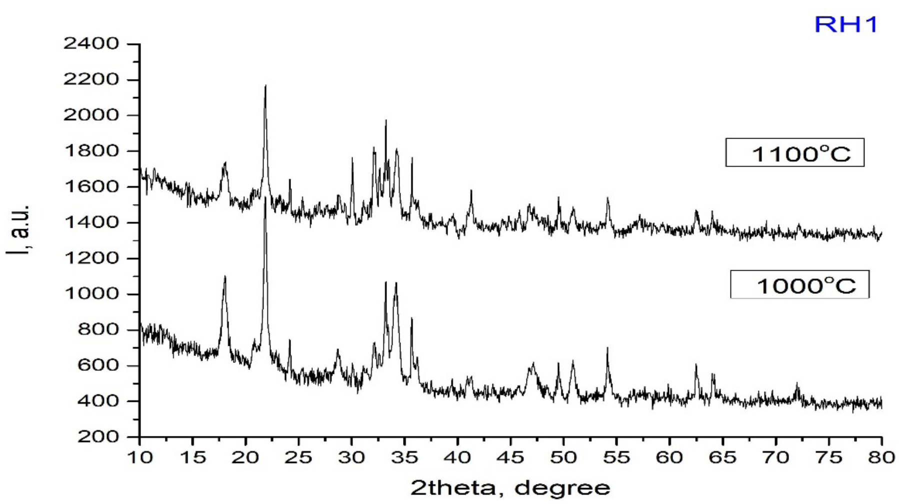

Fig. 5. X-ray analysis of garnet pigments with composition $3CaO.Fe_2O_3.3SiO_2$.

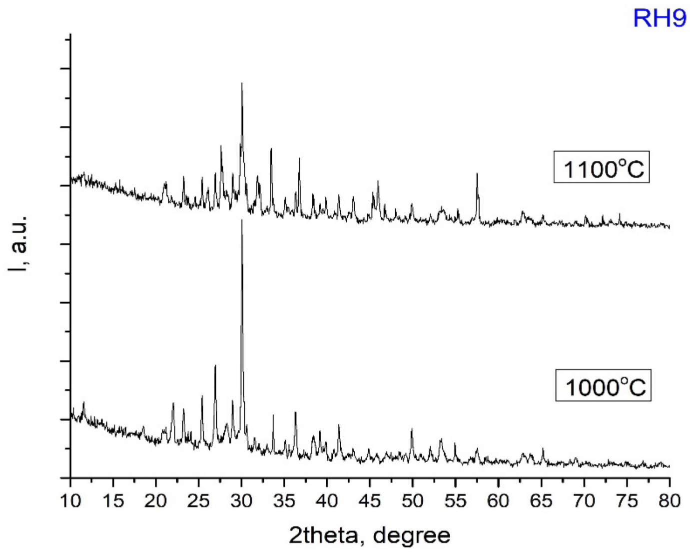

Fig. 6. X-ray analysis of garnet pigments with composition $3CaO.Cr_2O_3.3SiO_2$.

Table 3. Colour of the garnet pigments.

Sample	Colour	L	a*	b*
RH 1 / 1000°C		46.99	5.,87	10.81
RH 1 / 1100°C		43.15	4.92	9.96
RH 3 / 1000°C		83.46	-0.61	8.06
RH 3 / 1100°C		82,29	-2.29	19.63
RH 9 / 1000°C		62.29	-6.05	31.16
RH 9 / 1100°C		65.45	-12.53	39.39

a* = 5.87, b*= 10.81.

For the compositions with chromophore vanadium, the best results were obtained at RH 3 (synthesized at 1100°C) - b*= 19.63.

For the compositions with chromophore chromium, the best results were obtained at RH 9 (synthesized at 1000°C) where the amount of green colour (- a*) was the largest = -12.53. With the same composition, the largest amount of yellow colour (+ b*) is 39.39.

It is observed that the results in terms of colour saturation are very well for pigments with rice husk added. Probably, the impurities in the rice husks enhance the colours and make them stronger and more stable.

Hot Stage Microscopy analysis (HSM analysis)

Using Stage Microscopy method, it is possible to track the change in the thermal behavior of the materials, including of pigments. Fig. 7 - 9 show hot-stage microscopic analysis (HSM analysis) of compositions RH1, RH3 and RH9.

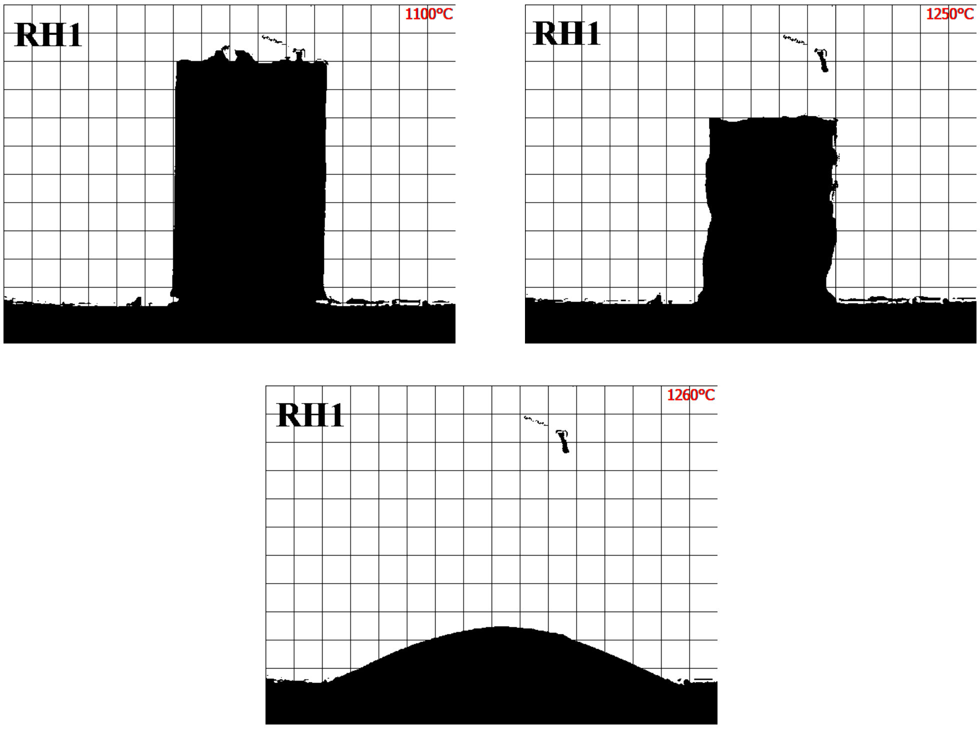

Fig.7. HSM analysis of RH1 composition at temperatures of 1100°C, 1250°C and 1260°C.

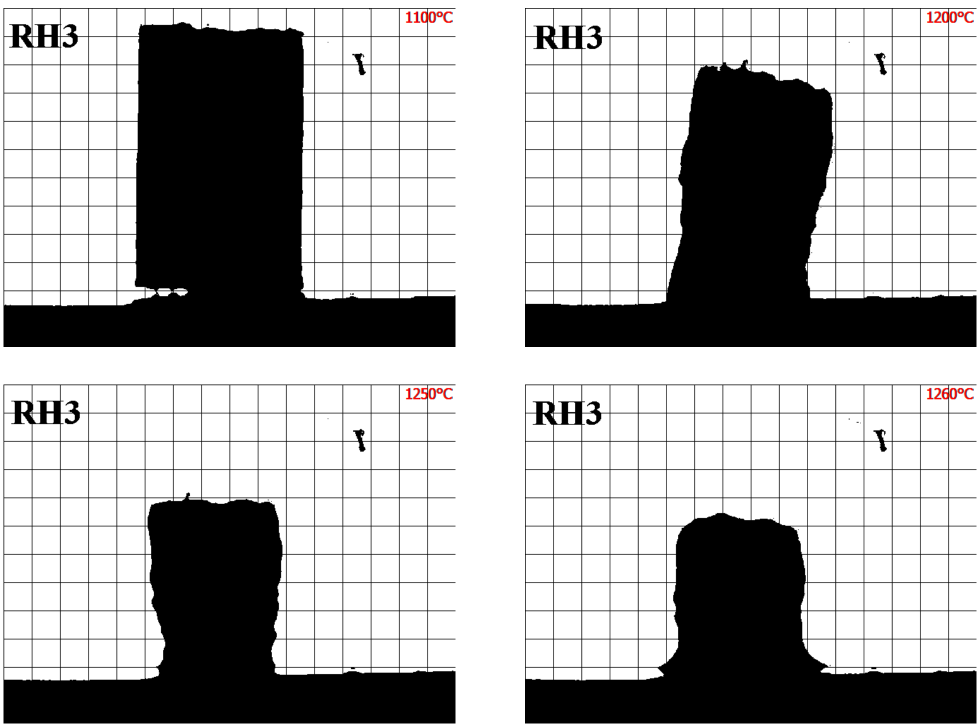

Fig. 8. HSM analysis of RH3 composition at temperatures of 1100°C, 1250°C, 1250°C and 1260°C.

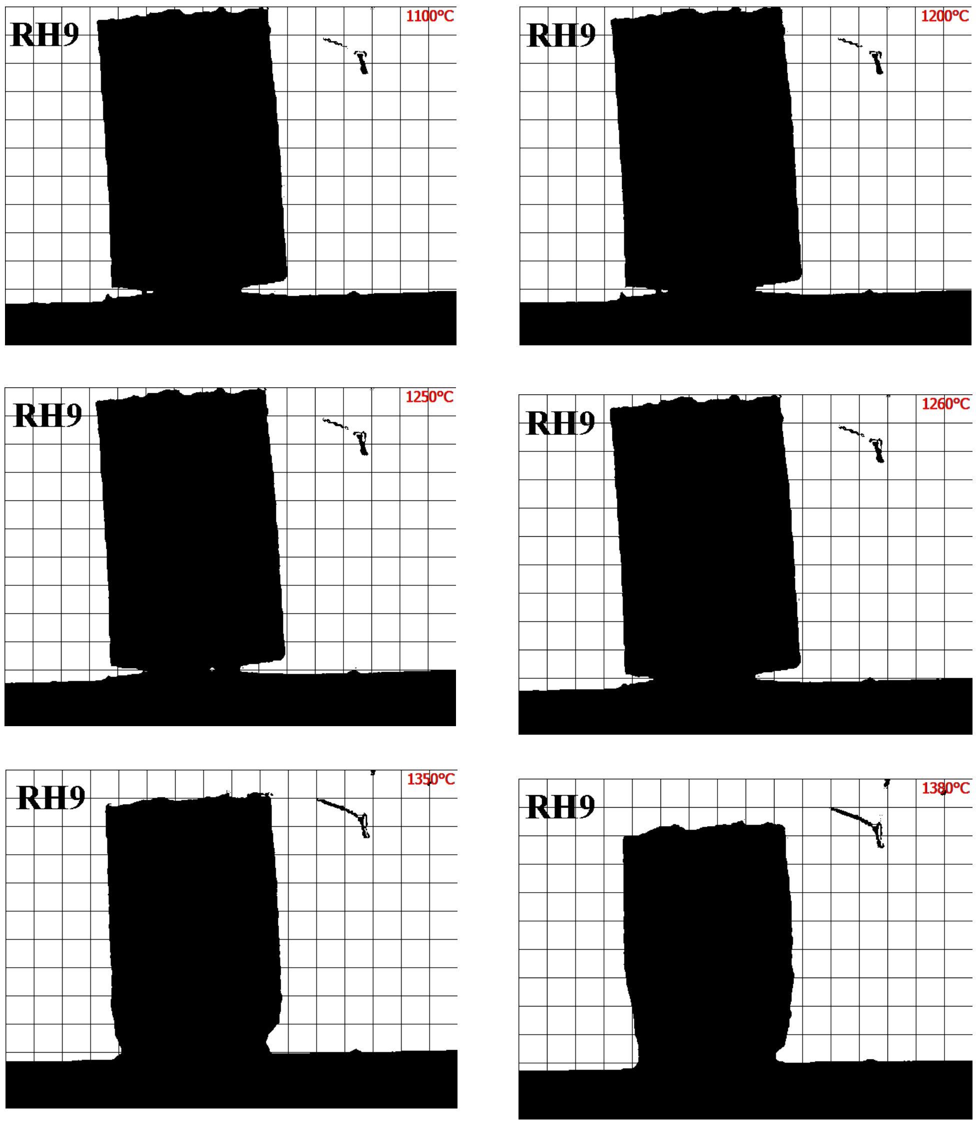

Fig. 9. HSM analysis of RH9 composition at temperatures of 1100°C, 1200°C, 1250°C, 1260°C, 1350°C and 1380°C.

The research conducted shows that at a temperature of 1260°C the pigments are spilled.

It can be seen from Fig. 6 that the pigments with composition RH3 are more stable than those with composition RH1. At a temperature of 1260°C, the pigments have not yet started to spill, unlike composition RH1.

Fig. 9 proves the great thermal stability of the synthesized pigments. Even at a temperature of 1380°C, the sample remains thermally stable. As can be seen, the sample RH9 - with the composition of uvarovite, obtained from burned waste rice husk are the most stable of the three types (RH1, RH3 and RH9), with the highest fire resistance and do not change even up to temperatures of 1380°C - 1400°C. This fact means that they can be added to ceramic glazes and used to glaze tiles and other ceramics without breaking down or reacting chemically with it.

CONCLUSIONS

- Garnet pigments were synthesized using the solid phase sintering method at two temperatures of 1000°C and 1100°C respectively. Oxidized rice husk ash was used as a substitute for pure SiO_2.
- Hot-stage microscopy studies show that almost all types of pigments are stable at high temperatures. The most stable being the pigments with composition RH9 (uvarovite) - these samples remain unchanged up to 1380°C - 1400°C.
- By a CIELab colour measurement system, the colour characteristics of the obtained garnet ceramic pigments were determined.
- Comparing the three compositions, it was found that the best results were obtained at: RH1 - synthesized at 1000°C, at RH 3 - synthesized at 1100°C, and at RH 9 - synthesized at 1000°C.

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