MINERAL AND SECONDARY CLAY RAW MATERIAL RESOURCES FOR OBTAINING HIGH-ALUMINUM MASSES

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ABSTRACT

The results of a study of the chemical, mineralogical composition, as well as IR spectroscopic and optical characteristics of promising clay raw materials of Uzbekistan, in particular kaolins of the AKF - 78, AKS - 30 grades of the Angrensky and kaolins of the Alyansky and bentonites of the Kasansky deposits of the Uzbekistan are presented. The recycling of alumina-containing waste from the Shurtan gas-chemical complex as an alumina-containing component is shown. The main physicochemical characteristics of the materials under study have been established and the possibilities of using them as the main clay component for developing the composition of high-alumina ceramic masses have been shown.

Keywords: kaolin, grades, bentonite, chemical, x-ray phase, optical, electron microscopic raster, IR spectra, high-alumina mass, alumina-containing catalyst.

INTRODUCTION

To produce high-alumina ceramics, kaolin rocks, which belong to the sillimanite group in the form of kaolinite, kyanite, sillimanite and andalusite, are mainly used as raw materials [1 - 3]. It should be noted that in addition to kaolinite ($Al_2O_3.2SiO_2.2H_2O$), the other three minerals have the same composition, corresponding to the formula $Al_2O_5.SiO_2$, which after firing at appropriate temperatures all turn into the mullite mineral.

According to their classification, mullite and mullite-corundum ceramic materials are classified as high-alumina; the aluminium oxide content in them must be at least 60 wt.%. It is impossible to develop a high-alumina ceramic composition from natural raw materials, in particular kaolin, due to small quantities of aluminium oxide.

Currently, Angren kaolin LLC (Tashkent region), based on kaolins from the Angren deposit, produces the following three grades of enriched kaolins: AKF - 78 and AKS - 30 [4, 5]. Enriched kaolin AKF - 78 is characterized by an average content of aluminium oxide in the range of 32 - 35 wt.%, iron oxide less than 1.0 wt.%, satisfactory molding properties, plasticity, binding ability, etc. The average content of aluminium oxide in the AKS-30 grade of kaolin is 25 - 30 wt.%, due to the presence of residual dispersed quartz sand, which affects its ceramic-technological properties - lower ductility, binding capacity and other indicators.

It is known that a high content of fine fraction of kaolin minerals increases plasticity, water content of masses and reduces the sintering temperature. Kaolins from different deposits of the Republic differ in chemical, mineralogical and granulometric composition, and, as a rule, are classified technologically.

Kaolins of the Alliance deposit is in the Samarkand region. The deposit is in favourable geological and geographical-economic conditions. The rock is soft in density, easily breaks or crumbles in the hands, and gets wet and blurry in water [6, 7].

The kaolinite content in it ranges from 20 to 50 wt. %. Kaolins have different colours: white, grey and yellow; in terms of their chemical and mineralogical composition, ceramic-technological and physical-mechanical properties, they are a valuable raw material for the ceramic industry. Their advantageous features are the constancy of the chemical and mineralogical composition, the low content of colouring oxides after enrichment and fairly high plasticity due to the presence of montmorillonite in their composition in an amount of 6.5 %. It should be noted that the granulometric composition of Alliance kaolins is represented mainly by particle sizes up to 0.005 mm - 80.51 %, which allows them to be characterized as highly dispersed kaolin. At the same time, the amount of fraction of this size in Angren kaolins is about 30 - 32 %. Based on this, compositions using Aliance kaolins have also been designed.

It should be noted that in the Republic there are no geological processed deposits of natural minerals in which the aluminium oxide content is higher than 35 - 40 wt.%. To increase the aluminium oxide content in the kaolin mass, it is necessary to add alumina-containing components [8 - 10]. It should be noted that at gas processing enterprises, large quantities of alumina-containing catalysts - zeolites are used to purify the natural gas produced, which are sent to dumps after the end of their service. The annual volumes of them sent to dumps amount to hundreds of tons, and at present it seems very promising to use them to produce high-alumina ceramic materials for various purposes.

EXPERIMENTAL

Materials

As potential and promising raw material sources to produce high-alumina ceramic materials, we used enriched kaolin produced by Angrenkaolin LLC, grades AKF - 78, AKS - 30 and Alliance kaolin, bentonite from the Kasanskoe deposits, as well as spent catalysts from the Shurtan gas chemical complex (ShGCC).

To conduct experiments, spent zeolite from the Shurtan Gas Chemical Complex (ShGCC) was used as technical alumina. This synthetic zeolite is a granular, highly porous molecular sieve intended for the technology of sorption purification of natural gas. Spent zeolites from ShGKhK in the initial state have an aluminosilicate composition, the amount of aluminium oxide is usually about 78 - 88 wt.%, sometimes in some types it reaches 90 wt.%. In this regard, this waste should be considered as an aluminous raw material for use as sintering components of high-alumina masses of ceramic materials.

Bentonites from the Kasan deposit in the Kashkadarya region were used as a plasticizing and binding component of the ceramic mass. This bentonite clay consists mainly of quartz, feldspar, plagioglaze, and clay minerals, including predominantly the following minerals: montmorillonite - 76.6 wt.%, hydromica - 22.7 wt. % and kaolinite - 0.7 wt. %.

Methods

Chemical analysis of samples of clay raw materials was carried out using standard silicate analytical methods [11].

The phase composition of the studied raw materials and fired experimental masses was determined by the X-ray method. Diffraction patterns were obtained using the powder method using a DRON - 4.0 installation, CuK radiation, and a Ni filter. The radiograph was taken at a rate of generally 2 deg min^{-1}. Monocrystalline quartz was used as an internal standard. In the calculations and identification of phases samples under study, we used tables and reference books compiled by the authors of the works [12 - 14], as well as the international card index on X - ray powder patterns [15].

IR spectroscopic study on a TI S50 IR-Fourier spectrometer (Thermo Fisher Scientific, USA) at each frequency 4000 - 400 cm^{-1}, with a spectral power of no more than 0.1 cm. When deciphering a sample of IR spectra, reference books were used [16, 17].

Morphological studies of the sample surface were carried out using a scanning electron microscope SEM - EVO MA 10 (Zeiss, Germany), using back-scattered electrodes Signal A = SE 1, under shooting conditions: voltage ENT - 15.0 kV, working distance WD - 8.5 mm. The description of the phase compositions and deciphering of the structural characteristics of kaolin samples were carried out using the reference book [18].

Thus, chemical-analytical, X-ray phase, microscopic and raster electron microscopic methods were used to identify the chemical and mineralogical compositions of clayey raw materials and secondary resources of Uzbekistan.

RESULTS AND DISCUSSION

Below are the physicochemical characteristics of the raw materials used to develop the composition of high-alumina ceramic masses, according to the method [19, 20]. The results of determining the chemical composition of the studied clayey raw materials of Uzbekistan for the development of the composition of high-alumina masses are given in Table 1.

The results of X-ray analysis (Fig. 1a and Fig.1b) of enriched kaolins of the AKF - 78 and AKS - 30 brands show that the diffraction patterns of the samples have a similar set of diffraction lines, the difference lies in the different ratio of the intensities of the diffraction lines of kaolinite and β-quartz. The intensity of the diffraction lines of β-quartz is significantly higher in the X - ray diffraction pattern of the AKS - 30 kaolin sample.

In the X-ray diffraction pattern of the AKF - 78 sample, lines of hydromica with interplanar distances d = 1.020 and 0.499 nm are visible in the region of smaller angles, which indicates only a small amount of the latter. On the X - ray diffraction patterns of these samples, diffraction lines with interplanar distances were established: - β-quartz - 0.424; 0.333; 0.245; 0.228; 0.223; 0.213; 0.198; 0.181; 0.154; 0.138; 0.137 nm and kaolinite - 0.711; 0.434; 0.356; 0.279; 0.249; 0.234; 0.228; 0.198; 0.179; 0.166 nm.

In the X - ray diffraction patterns (Fig. 1c) of enriched Alliance kaolin, diffraction lines appear, related to the mineral kaolinite (0.255; 0.443; 0.496 nm), in all ranges of the reflection angle, their intensity increases significantly [21].

The diffraction maxima of β - quartz (0.166; 0.181; 0.197; 0.212; 0.227; 0.227; 0.244; 0.333; 0.422 nm) slightly decrease in intensity; the diffraction maxima of hydromica in enriched kaolin disappear completely. The nature of the lines of interplanar distances in the X - ray diffraction pattern of enriched Alliance kaolin indicates a significant increase in the content of the mineral kaolinite and a decrease in the amount of β - quartz.

X-ray phase studies of samples of Kasansky bentonite (Fig. 3d) showed the presence of mont-morillonite clay minerals - lines corresponding to d = 1.016; 0.99; 0.443; 0.255; 0.245; 0.224; 0.168 nm and hydromica d = 0.628; 0.403; 0.398; 0.375; 0.370 nm. Since some parts of the manifestation are significantly sandy, and distinct intense effects of β-quartz are

Table 1. Results of chemical analysis of the studied raw materials for high-alumina masses.

Name of raw materials	Mass content of oxides per air-dry substance, wt.%											LOI, wt.%
	SiO_2	Al_2O_3	Fe_2O_3 general	including		TiO_2	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3 general	
				Fe_2O_3	FeO								
Kaolin grade AKF - 78	51.72	31.96	0.57	0.37	< 0.20	0.52	< 0.30	1.05	0.06	0.31	0.07	0.32	12.53
Kaolin grade AKS - 30	57.42	26.50	0.68	0.66	< 0.20	0.50	< 0.30	1.15	0.47	0.16	0.06	1.31	12.02
Aliance kaolin enriched	51.25	34.80	0.49	0.30	0.19	0.31	0.38	0.46	0.22	1.41	0.02	0.47	10.19
Kaolin enriched High-alumina waste from Shurtan Gas Chemical Complex (ShGCC)	3.94	85.28	1.60	0.95	0.65	0.85	1.32	1.23	0.60	0.17	0.01	< 0.10	4.95
ShGCC calcined at a temperature of 1300°C	1.35	96.11	0.90	0.74	0.16	0.34	0.68	0.35	0.20	0.05	traces	traces	0
Kasan bentonite	55.83	17.64	5.39	5.50	0.39	0.72	0.20	1.26	2.70	2.64	0.28	0,84	12.30

Note: loss on ignition (LOI) includes: hygroscopic, constitutional, crystallized water, organic and volatile matter and carbon (IV) oxide.

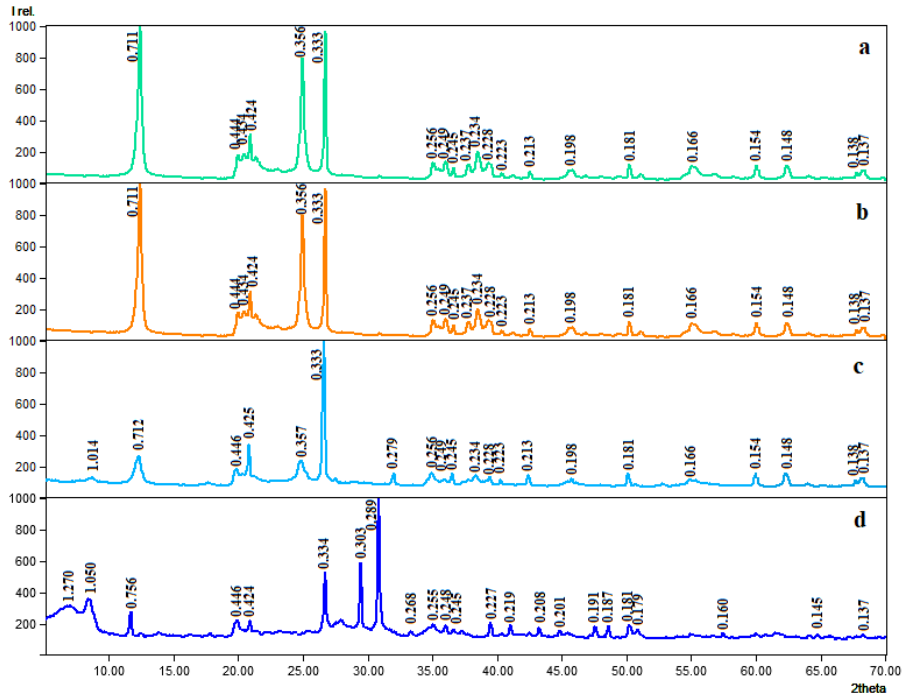


Fig. 1. X - ray diffraction patterns of clay raw materials where: (a) kaolin grade AKF - 78; (b) AKS - 30; (c) Aliance kaolin; (d) Kasan bentonite.

observed in the X - ray diffraction patterns with corresponding interplanar distances d = 0.426; 0.341; 0.246; 0.198; 0.184 nm and low-intensity lines related to the mineral kaolinite d = 0.712; 426; 0.228; 0.201; and 0.166 nm.

X-ray phase analysis determined the amount of the main rock-forming minerals of bentonite clays of the Kasansky deposits, which consist mainly of the mineral's montmorillonite - 76.6 wt.%, hydromica - 22.7 wt.% and kaolinite - 0.7 wt.%.

X-ray diffraction patterns of samples of high-alumina waste from the Shurtan gas chemical complex (Fig. 2a) represent a diffraction pattern composed of a set of diffraction lines of hydroxide and γ-Al_2O_3 oxide.

The diffraction lines are characterized by large broadening, which is evidence of an imperfect defective crystal lattice, apparently due to prolonged exposure to temperature on the original aluminium hydroxide during operation. Based on the results of deciphering the X - ray patterns, it was established that they contain a mixture of two minerals with the corresponding sets of interplanar distances: γ - $Al_2O_3 \cdot H_2O$ - d = 0.620; 0.316; 0.234; 0.205; 0.185; 0.165; 0.152; 0.145; 0.143; 0.138; 0.131 nm and γ - Al_2O_3 - d = 0.284; 0.273; 0.256; 0.244; 0.231; 0.226; 0.202; 0.191; 0.179; 0.154; 0.148; 0.145; 0.138 nm.

X-ray diffraction patterns of the products of calcination of ShGCC waste samples (Fig. 2b) show that the products of heat treatment at a temperature of 1100 - 1200°C is mullite and corundum minerals, which are the main crystalline phases of high-alumina ceramic materials. In addition, calcination of the spent ShGCC catalyst also produces intermediate minerals - alumina and melilite.

Based on the results of IR spectroscopic analysis, it was established (Fig. 3) that kaolins of the AKF - 78, AKS - 30, Alliance grades, as well as Kasan bentonites belong to silicate minerals with layered structures. The obtained IR absorption spectra are similar to the spectra of similar known layered aluminosilicate minerals. In the IR spectra of these kaolins, absorption bands were detected in the regions 430 - 550; 640 - 820; 830 - 920; 970 - 1120; 1380 - 1430; 3400 - 3600 cm^{-1}, and the highest frequency and most intense bands are those in the regions 640 - 820; 970 - 1120 and 1380-1430 cm^{-1}, related to the vibrations of the bridge bond AI-O, Si-O, Si-O-Al. The absorption bands in the region of 3400 - 3600 cm^{-1} are due to stretching vibrations of the OH group bond.

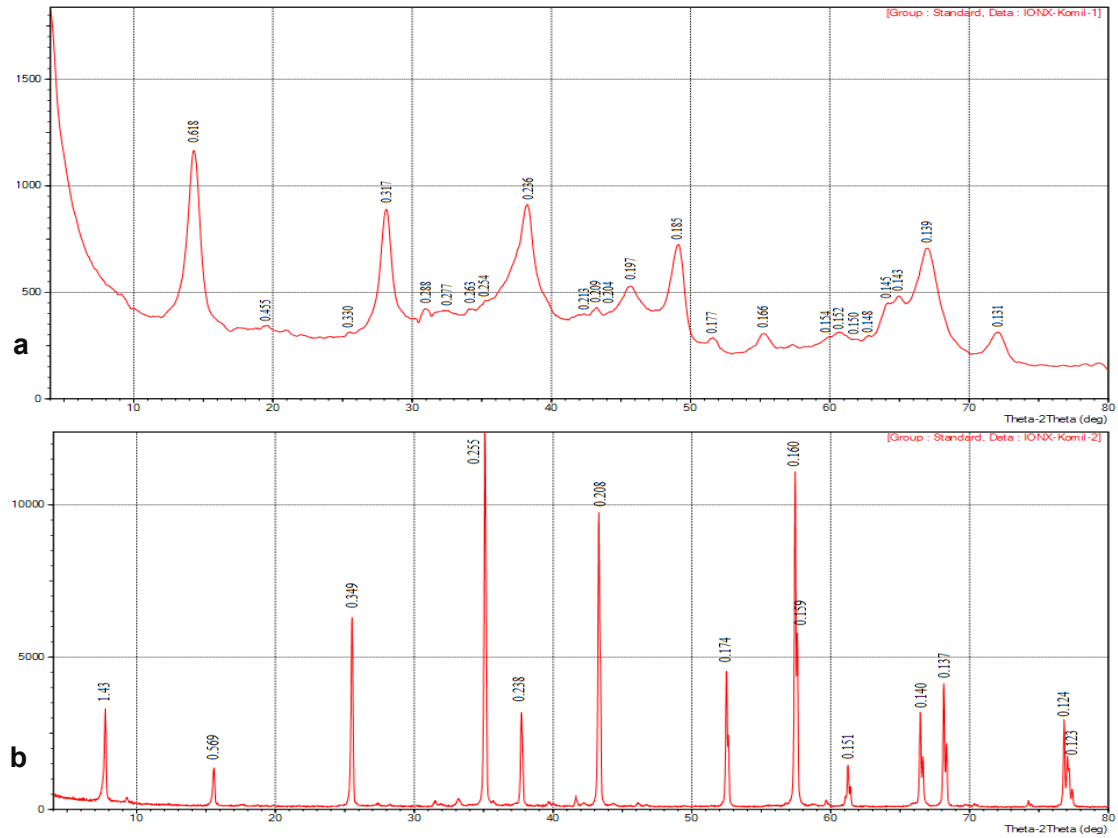


Fig. 2. X - ray diffraction patterns of the initial (a) and calcined (b) high-alumina waste from the ShGCC.

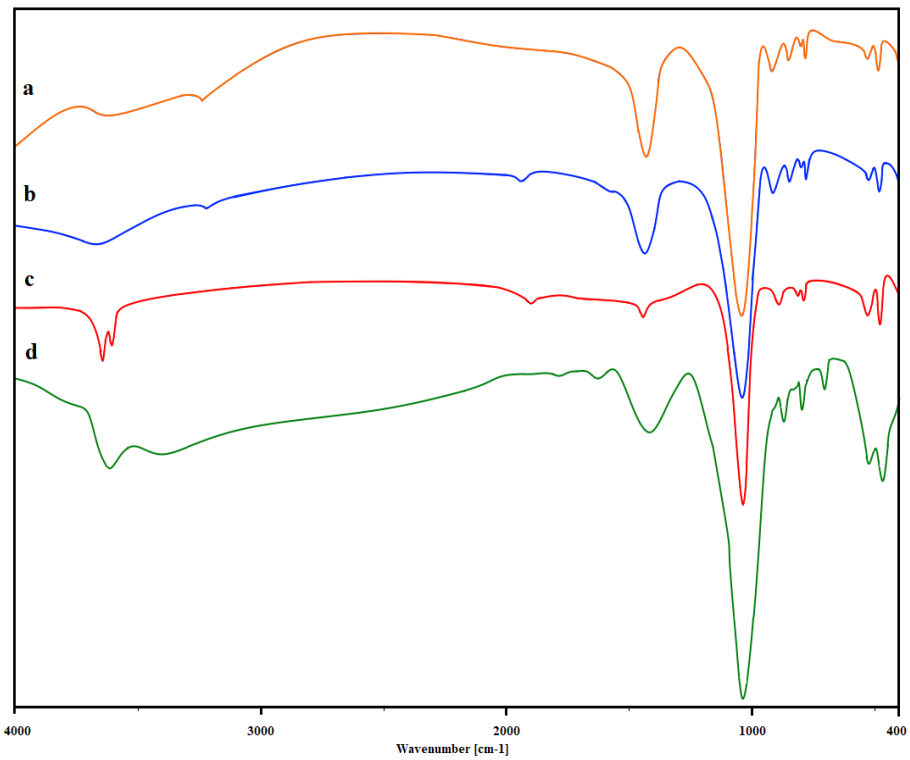
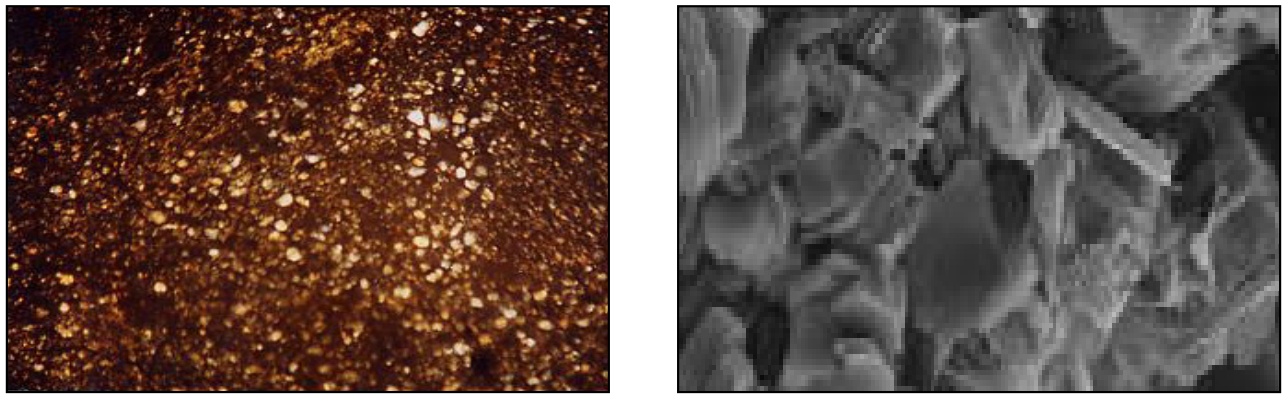


Fig. 3. IR spectrum curves of kaolin grade AKF - 78 (a), AKS - 30 (b), Alliance (c), Kasan bentonite (d).



a b

Fig. 4. Microscopic (a) and electron microscopic raster (b) images of Alliance kaolin.

Table 2. Physico-chemical properties of raw material samples.

Name of raw materials	True density, kg m^{-3}	T_{mel}, °C	Mineralogical composition
Kaolin AKF-78	2.57×3^{10}	1760	kaolinite, β - quartz
Kaolin AKS-30	2.5×3^{10}	1640	kaolinite, β - quartz
Kaolin Alliance	2.58×3^{10}	1730	kaolinite, β - quartz, feldspar, montmorillonite
Aluminous waste from ShGCC	3.06×3^{10}	2050	aluminum hydroxide, gamma alumina
Kasan bentonite	1.89×3^{10}	1210	montmorillonite, hydromica, kaolinite, β - quartz

Based on the results of petrographic analysis, Alliance kaolins are kaolinite-hydromica clay with a sandy admixture of quartz, of heterogeneous composition (Fig. 4a). The structure is finely scaly, the size of the scales is generally smaller than 0.01 mm, but their main mass is larger than 0.001 mm. The shape of the scales is represented by very rare hexagonal cuts. The texture is heterogeneous and knotty, weakly pseudolayered, which is due to the alternation of clay aggregates of different structural types. However, the latter are not ideally oriented, as evidenced by the absence of simultaneous extinction and brightening and the frequent multidirectionality of grains.

A scanning electron microscopic image of enriched kaolin shows pseudohexagonal-shaped crystals collected in separate packets with a layered structure (Fig. 4b). The layered structure of the main mineral, kaolinite, and the polymineral composition of the clay are clearly visible. In addition to the minerals of the kaolinite group, associated minerals are present: quartz, carbonates and montmorillonite and halloysite.

The physicochemical properties of the studied samples of samples of the studied raw materials are given in Table 2.

CONCLUSIONS

Thus, physicochemical studies of promising clay raw materials and secondary resources were carried out to develop the composition of high-alumina ceramic masses, such as Angren kaolin grades AKF - 78, AKS - 30, Alyansky kaolin, alumina-containing waste of the Shurtan gas chemical complex and Kasansky bentonite, deposits of Uzbekistan. The chemical and mineralogical compositions, optical and IR spectroscopic characteristics of the materials under study were determined using chemical-analytical, X - ray phase and microscopic, electron microscopic analyses and the possibility of using them as the main component of high-alumina ceramic masses is shown.

Authors' contribution

A.A.E.: Conceptualization of the study, data analysis and X-ray phase analysis; Z.R.K.: Discussion and interpretation of physico-chemical research results and manuscript preparation; O.O.J.: Experimental design, sample preparation; A.M.E.: Conducting microscopic and spectroscopic studies, validation of experimental results.

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