



Natural CaO-TiO₂-SiO₂ based ceramics

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Abstract

Lešnica river deposits consist of a large number of minerals of different grain sizes including sphene. Since it is very difficult to obtain pure monophase titanite by different synthetic routes (sol-gel, coprecipitation, combustion, spray pyrolysis and hydrothermal method), the aim of this work was to study the structure of the sphene from the Lešnica river deposits and possibility of using it as a natural precursor for CaO-TiO₂-SiO₂ based ceramics. The sphene from Lešnica was analyzed by different methods: tris-timulus colorimetry, infrared spectroscopy, electron microprobe and X-ray single crystal diffraction. It was confirmed that Al, Fe, Mn and P are present in the sphene structure and proposed that corresponding structural formula could be: $(Ca^{2+}_{1.008} Mn^{2+}_{0.002})_{1.010} (Ti^{4+}_{0.901} Fe^{3+}_{0.033} Al^{3+}_{0.060} P^{5+}_{0.001})_{0.995} Si^{4+}_{1.024} O^{2-}_5$.

Keywords: sphene, natural precursor, structure analysis

I. Introduction

Sphene or titanite is nesosilicate mineral with monoclinic symmetry and empirical formula CaTiSiO₅ [1]. Translucent to transparent varieties of this mineral can be used as precious and semiprecious gems. Titanite also has a good thermal stability and it is an excellent candidate for a host lattice of ceramic materials [2]. Since it is possible to incorporate a variety of elements into its crystal lattice, it can also be used for immobilization of radioactive nuclear waste [3] or luminescent materials. Titanites containing Cr³⁺ are used as pink pigment for painting ceramics in pink and purple [4]. In high concentrations sphene is a potential source of titanium.

Sphene crystallizes in monoclinic prismatic class 2/m in the space group $P2_1/a$ and $A2/a$. Unit cell parameters are $a = 0.656$ nm, $b = 0.872$ nm, $c = 0.744$ nm, $\beta = 119.716^\circ$, $Z = 4$. In work on synthetic sphene Speer and Gibbs [5] reported that the original unit cell parameters and space group $C2/c$ [6] were transformed into new values characteristic for space group $A2/a$ [7]. The axial transformation from Zachariasen's $C2/c$ cell to Mongiorgi and Riva di Sanseverino's $A2/a$ cell is (transforma-

mation matrix) (101/010/-100) [8]. Later, the proposed space group was $P2_1/a$ [9]. However, the structure was first solved by Zachariasen [6], who proved that this mineral is composed of isolated tetrahedra [SiO₄] and groups [CaO₇] and [TiO₆].

The ideal chemical formula of sphene can be written as CaTiO(SiO₄), but within the structure significant substitutions on both cation and anion sites may occur. In their study Deer *et al.* [10] found that calcium, in coordination 7, can be replaced by strontium, barium, rare earth elements and thorium when high valence is compensated by joining the trivalent iron and aluminum in place of titanium. Titanium in the structure can be replaced with Al³⁺ [11], Fe³⁺ [12], Ta⁵⁺ [13] and Nb⁵⁺ [14] when the charge difference is compensated by incorporating Na⁺ instead of Ca²⁺. Of great importance for natural sphene are the substitution pairs (Al, Fe)³⁺ with Ti⁴⁺ and simultaneously (OH, F)⁻ with O²⁻, where the total content of Al + Fe is not more than 30 mol% and that aluminum always dominates [15]. Dual substitution of Fe³⁺ and Al³⁺ with Ti⁴⁺ and OH⁻, Cl⁻, F⁻, with O²⁻, are only possible in natural sphene [5]. It was noted that all titanium cations in octahedral chain moved in the same direction along the axis a . These cations are moved out from their geometric centre in octahedrons, which is reflected in structure geometry i.e. longer and shorter

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Ti–O bonds [16]. The TiO_6 octahedra are strongly distorted and as the consequent low point symmetry is desirable to develop an intense colouration [17] for instance, chromium in malayaite (CaSnSiO_3) gives rise to a characteristic pink shade that turns to be purple in cassiterite (SnO_2) and brown in titanite.

The investigated sphene was separated from the Lešnica river deposits in Cer ore field. Besides cassiterite as the most common mineral component, there is an increased portion of minerals with significant content of niobium and tantalum, then rutile, magnetite, rarely monazite, a very rare torite, euksenite, allanite, scheelite, apatite, spodumen and other minerals [18].

The most widespread rock in the studied Cer ore field is quarconconite. It is mostly dark green and it mostly contains quartz, orthoclase, andensite, biotite and hornblende. Secondary minerals are sphene, apatite, ortite, zircon, rutile and magnetite. Amphibolite gneiss lies at the base of Cer and appears only in the deeper creeks. The rock has completely gneiss structure with grey colour because of the enrichment with the ferro-magnesium components. Radiant, yellow sphene crystals can be seen macroscopically. Microscopic constituents of gneiss are: biotite, hornblende, orthoclase, plagioclase, quartz, magnetite, zircon, apatite, sphene, allanite, epidote and chlorite [19].

Because it is very difficult to obtain pure synthetic monophasic titanite by sol-gel, coprecipitation, combustion, spray pyrolysis and hydrothermal methods, the aim of this work was to study the structure of the sphene from the Lešnica river deposits and its possibility of being used as a natural precursor for synthesis $\text{CaO-TiO}_2\text{-SiO}_2$ based ceramics.

II. Experimental methods

Sphene crystals were extracted from the Lešnica river deposits in a few steps. The 0.25–0.5 mm fraction, where sphene is most commonly found, was separated in the first step. For further separation heavy liquids method (bromoform) was used. Sphene crystals that were found in association with cassiterite, garnet, apatite and zircon in heavy nonmagnetic fraction were separated with Frantz's isodynamic separator with the current power of 1.2 A and the lateral slope of 5° (in further text *Sample-1*). Yellow letter like form crystals, observed under the binocular microscope, were hand-separated, cutted for further analysis and two samples were obtained: *Sphene-1* and *Sphene-2*. The monocrystals *Sphene-1* and *Sphene-2* were selected for chemical analysis and X-ray studies and crystals selected from the *Sample-1* were used for other characterization methods.

Density of the selected minerals from fraction of the *Sample-1* was measured with pycnometer method. Colour of sphene from fraction of the *Sample-1* was determined on the instrument SPEKOL brand Carl Zeiss Jena with the unit for reflection R45/0 (MgO was used

as a standard). Sphene was identified with Infrared (IR) spectroscopy. Pellets were made from the *Sample-1* and KBr and analysed on IR-spectrophotometer Perkin Elmer Model 597. Experiments were performed for the range of wavenumber from 200 and 4000 cm^{-1} and at the recording time of 4 minutes. The sphene crystals from the *Sample-1* were also analyzed on JEOL 8100 electron microprobe. X-ray diffraction (XRD) analysis of both sphene crystals was performed on the single crystal diffractometer brand Syntex P1 equipped with X-ray tube with molybdenum anode ($\lambda = 0.0711\text{ nm}$). X-rays were passed through a collimator diameter of 0.5 mm. Orientation matrix and unit cell dimensions were determined using an autoindexing procedure. Because sphene can crystallize in two space groups, structure of both crystals is refined by least squares procedure in the space groups $C2/c$ and the $P2_1/c$ with the SHELXL-97 software package from Wingx32 [20]. For the graphical representation of the complete structure computer program ATOMS was used [21].

III. Results and discussion

The sphene single crystals from the Lešnica river deposits were transparent, yellow and radiant. Dimensions of the crystals were: $d_{\min} = 0.095\text{ mm}$, $d_{\max} = 0.1960\text{ mm}$, $d_{\text{mean}} = 0.14\text{ mm}$ (*Sphene-1*), $d_{\min} = 0.1140\text{ mm}$, $d_{\max} = 0.2320\text{ mm}$, $d_{\text{mean}} = 0.15\text{ mm}$ (*Sphene-2*). Wavelength $\lambda = 581\text{ nm}$ on the chromatic diagram (Fig. 1.) belongs to the range of yellowish orange colour [22]. This colour is common for natural sphene.

The density of the sphene obtained by pycnometer and from the X-ray diffraction crystal structure refinement is 3.81 g/cm^3 and 3.54 g/cm^3 , respectively. Density calculated from the refinement was in correlation with

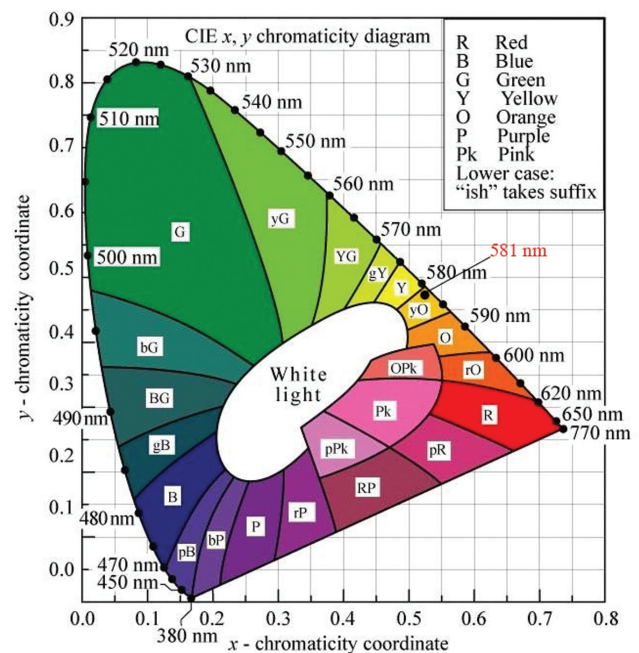


Figure 1. Chromatic diagram of sphene [22]

Table 1. Sphene chemical composition obtained from microprobe

	Oxide content, C [wt.%]	Molecular mass, M [g/mol]	C/M	Cation content- K	Anion O ⁻² content	K × f*
SiO ₂	31.38	60.084	0.522	0.522	1.045	1.024
CaO	28.84	56.077	0.514	0.514	0.514	1.008
TiO ₂	36.75	79.898	0.460	0.460	0.920	0.902
Fe ₂ O ₃	1.34	159.691	0.008	0.017	0.025	0.033
Al ₂ O ₃	1.56	101.961	0.015	0.031	0.046	0.060
P ₂ O ₅	0.05	141.943	0.001	0.001	0.002	0.001
MnO	0.08	70.937	0.001	0.001	0.001	0.002
Σ	100				2.553	

*f = 5 / 2.553 = 1.958

Table 2. Crystallographic data of sphene with estimated standard deviation (in parentheses)

	Sphene-1 A2/a	Sphene-1 P2 ₁ /a	Sphene-2 A2/a	Sphene-2 P2 ₁ /a
a [nm]		0.6551(1)		0.7052(2)
b [nm]		0.8699(1)		0.8698(2)
c [nm]		0.7055(1)		0.6547(1)
α [°]			90	
β [°]			113.84(1)	
γ [°]			90	
volume [nm ³]		36.77 (1)		36.74 (1)
Z			4	
wavelength [nm]			0.071073	
2θ [°]			4.13–29.52	
No. of measured reflections		6075		3467
Unique data	502		500	983
R ₁ (I > 2σ(I))	0.035	0.042	0.029	0.031
wR ₂ (I > 2σ(I))	0.121	0.121	0.082	0.089
R ₁ (all reflections)	0.035	0.048	0.028	0.041
wR ₂ (all reflections)	0.121	0.128	0.081	0.097
Goof = S	1.240	1.108	1.201	1.144

the literature data (3.45–3.55 g/cm³) [10], while this is not the case with the density obtained by pycnometer. The density measured by pycnometer is slightly higher than the calculated density of sphene (7%). This is

caused by contamination of the specimen prepared for pycnometer by other higher-density minerals, such as cassiterite.

Infrared spectroscopy confirmed that the investigated phase in the samples was sphene (Fig. 2). Vibrations centred at about: 861 cm⁻¹, 714 cm⁻¹, 561 cm⁻¹, 432 cm⁻¹ and 334 cm⁻¹ are in good agreement with data published for sphene [23,24].

The results of chemical analysis are given in Table 1. Earlier geological and mineralogical studies have shown that the sphene from Lešnica may occur in quarconconite and gneiss. The investigated sphene was derived from amphibole gneiss. The chemical composition of the investigated sphene was compared with the chemical composition of sphene from eight independent samples [10] and confirmed a good agreement with the sphene from gneiss.

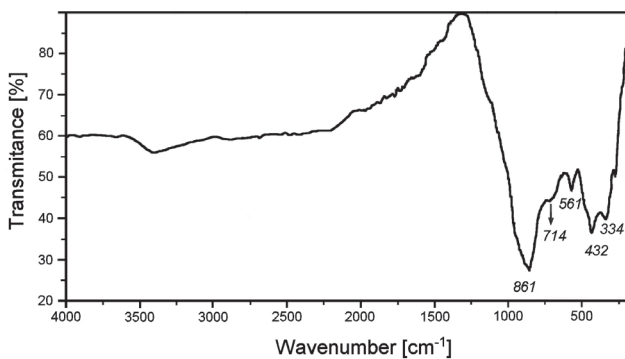
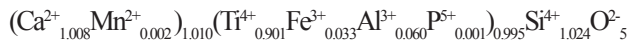


Figure 2. Infrared spectrum of sphene

Microprobe chemical analysis showed presence of Al, Fe, Mn and P in the sphene structure. The analysis showed the expected high content of major elements of given empirical formula (CaTiSiO₅) and small but not negligible content of Al and Fe. It can be assumed that these elements are replacing silicon and/or titanium in the empirical formula. Other elements, such as: Na, Mg, Mn and P are present in trace amounts. It is assumed that Mn is in the form of Mn²⁺ and exchange Ca²⁺ with similar ionic radii. Thus, structural formula obtained from microprobe chemical analysis could be:



The crystal structure was determined by X-ray single crystal diffraction. The structures were refined in

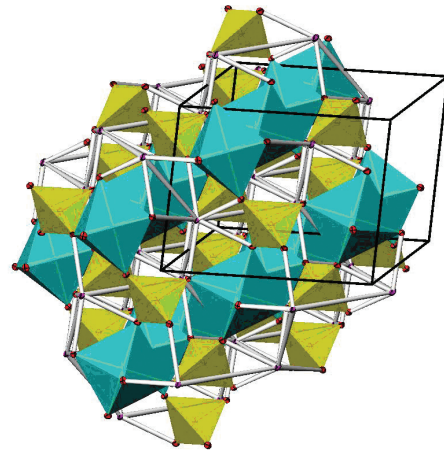


Figure 3. Polyhedral representation of structure for *Sphene-2 P21/a* (obtained with computer program ATOMS)

Table 3. Fractional atomic parameters and equivalent anisotropic temperature factors $U(eq)$ with estimated standard deviation (in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	$U(eq)$
<i>Sphene-1 A2/a</i>				
Ti(1)	0.5000	-0.5000	0.5000	0.011(1)
Ca(1)	0.7500	-0.1680(1)	0.5000	0.014(1)
Si(1)	0.7500	-0.3173(1)	1.0000	0.006(1)
O(1)	0.8821(3)	-0.2106(2)	0.8972(3)	0.008(1)
O(2)	0.7500	-0.4287(3)	0.5000	0.009(1)
O(3)	0.5894(2)	-0.4338(2)	0.8146(3)	0.009(1)
<i>Sphene-1 P2₁/a</i>				
Ti(1)	0.7501 (1)	0.2506(1)	0.5020(1)	0.011(1)
Ca(1)	0.7497(1)	0.5820(1)	0.7510(1)	0.014(1)
Si(1)	0.7500(1)	0.9327(1)	0.7498(1)	0.005(1)
O(1)	0.3531(3)	0.5393(2)	0.6179(3)	0.008(1)
O(2)	0.8528(3)	0.0393(2)	0.6180(3)	0.008(1)
O(3)	0.9357(3)	0.8163(2)	0.9106(3)	0.008(1)
O(4)	0.5651(3)	0.8162(2)	0.5894(3)	0.009(1)
O(5)	0.7500(3)	0.3213(2)	0.7500(2)	0.009(1)
<i>Sphene-2 A2/a</i>				
Ti(1)	0.5000	0.0000	0.0000	0.011(1)
Ca(1)	0.7500	-0.3320(1)	0.0000	0.014(1)
Si(1)	0.7500	-0.6827(1)	0.5000	0.006(1)
O(1)	0.6182(2)	-0.7893(1)	0.1028(2)	0.008(1)
O(2)	0.5893(2)	-0.5663(2)	-0.1854(2)	0.009(1)
O(3)	0.7500	-0.0715(2)	0.0000	0.009(1)
<i>Sphene-2 P2₁/a</i>				
Ti(1)	0.5018 (1)	0.2506(1)	0.7500(1)	0.011(1)
Ca(1)	0.7511(1)	0.5821(1)	0.7496(1)	0.015(1)
Si(1)	0.7498(1)	0.9327(1)	0.7499(1)	0.006(1)
O(1)	0.6183(2)	0.0392(2)	0.8532(3)	0.008(1)
O(2)	0.6183(2)	0.5394(2)	0.3530(3)	0.009(1)
O(3)	0.9107(2)	0.8162(2)	0.9355(3)	0.009(1)
O(4)	0.5893(2)	0.8162(2)	0.5647(3)	0.009(1)
O(5)	0.74984(2)	0.3214(2)	0.7496(3)	0.009(1)

space groups $C2/c$ and the $P2_1/c$, and then transformed into the new space groups $A2/a$ and $P2_1/a$, to comply with the regulations set by the Commission for the crystallographic data of the International Union of Crystallography. Comparing the output files in Wingx in the space group $A2/a$ and $P2_1/a$ it was found that space group $P2_1/a$ has much less forbidden reflections than space group $A2/a$, and therefore is more suitable for this crystal. On the basis of the statistical indicators of the quality of the refinement (R -value, $Goof$, residual electron density on differential $F_o - F_c$ map), the structure for

this sphene was established in the space group $P2_1/a$. All essential crystallographic parameters, the details of the structure determination and the experimental data processing are given in Table 2.

First were refined positions of atoms and thermal vibration parameters, and the parameter for extinction. For all atoms, thermal vibration parameters were refined anisotropic. Both space groups were transformed into new space group $A2/a$ and $P2_1/a$. The results of the refinements are presented in Tables 3 and 4. Table 3 shows fractional atomic parameters and equivalent anisotropic

Table 4. Interatomic distances (experimental and literature data [11]) with estimated standard deviation (in parentheses)

Bond	Experimental values [nm]	Literature values [nm]
<i>Sphene A2/a</i>		
Ti – O3	0.1870(1)	0.1868(1)
Ti – O3	0.1870(1)	0.1868(1)
Ti – O2	0.1981(1)	0.1976(2)
Ti – O2	0.1981(1)	0.1976(2)
Ti – O1	0.2013(1)	0.2009(2)
Ti – O1	0.2013(1)	0.2009(2)
Ca – O3	0.2266(2)	0.2269(3)
Ca – O2	0.2408(1)	0.2397(2)
Ca – O2	0.2408(1)	0.2397(2)
Ca – O1	0.2412(1)	0.2409(2)
Ca – O1	0.2412(1)	0.2409(2)
Ca – O1	0.2626(1)	0.2627(2)
Ca – O1	0.2626(1)	0.2627(2)
Si – O2	0.1635(1)	0.1631(2)
Si – O2	0.1635(1)	0.1631(2)
Si – O1	0.1638(1)	0.1634(2)
Si – O1	0.1638(1)	0.1634(2)
<i>Sphene P2₁/a</i>		
Ti – O5	0.1855(2)	0.1768(2)
Ti – O5	0.1884(2)	0.1970(2)
Ti – O3	0.1979(2)	0.1979(2)
Ti – O4	0.1985(2)	0.1985(2)
Ti – O1	0.2012(2)	0.2012(2)
Ti – O2	0.2013(2)	0.2013(2)
Ca – O5	0.2268(2)	0.2275(4)
Ca – O4	0.2407(2)	0.2501(7)
Ca – O1	0.2407(2)	0.2354(9)
Ca – O3	0.2408(2)	0.2707(7)
Ca – O2	0.2414(2)	0.2322(6)
Ca – O2	0.2619(2)	0.2472(9)
Ca – O1	0.2632(2)	0.2549(10)
Si – O4	0.1633(2)	0.1594(7)
Si – O3	0.1636(2)	0.1648(9)
Si – O2	0.1638(2)	0.1671(9)
Si – O1	0.1642(2)	0.1625(12)

temperature factors $U(eq)$. Table 4 shows interatomic distances compared with literature data. The experimental results are compared with published data from Grisons sphene [11] because of similarities in chemistry. The distances Ti-O, Si-O, Ca-O in space group $A2/a$ show good agreement with literature data [5,11]. Unit cell for *Sphene-2* $P2_1/a$ is presented in Fig. 3. Displacement of Ti from the centre of the octahedra is very small (almost imperceptible) only when structure model in space group $P2_1/a$ was applied.

IV. Conclusions

River drift Lešnica, from which sphene crystals are separated for analysis, consists of a large number of minerals with different grain sizes. Sphene crystals were found in the 0.25 mm to 0.5 mm grain size fraction, in association with cassiterite, garnet, apatite, zircon and other minerals. Due to the complexity of the process of sphene formation, as well as its appearance in different types of rocks and isomorphism with Sn and V in place of Ti, a cation exchange could appear. Chemical analysis confirmed that Al, Fe, Mn and P were present in the sphene from the Lešnica river deposits in addition to basic elements. Considering the ionic radii, it was assumed that Al, Fe and P were replacing Ti and Mn was replacing Ca in the sphene structure. The crystal structure was analysed by X-ray single crystal diffraction and the obtained XRD patterns were refined by the SHELXL-97 software package. On the basis of the statistical indicators of the quality of the refinement the structure for the investigated sphene was established in the space group $P2_1/a$. Consequently, it seems that the sphene from the Lešnica river deposits could be used as a natural precursor for synthesis of CaO-TiO₂-SiO₂ based ceramics.

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