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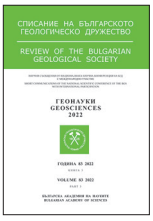

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Crystal structure of scapolite from Samurski Dol, Chepelare region, Central Rhodopes, Bulgaria

Кристална структура на скаполит от Самурски дол, Чепеларе, Централни Родопи, България

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Abstract. Samples of scapolite from the marble quarry from the Samurski Dol locality, situated nearby Chepelare, Central Rhodopes, Bulgaria have been subjected to chemical analyses and single crystal X-ray diffraction studies. The obtained values for the meionite component (*Me*) range between 70 and 75. The crystal structure of the studied sample has been solved in both *I*4/*m* and $P4_2/n$ space groups, traditionally assigned to scapolite members. The paper provides new insight on the choice of correct space group for description of scapolites crystal structures, with a view of the preferred positions by silicon and aluminum ions and their framework ordering.

Keywords: scapolite, single-crystal X-ray analysis, space group.

Introduction

Scapolites are rock-forming minerals with well-pronounced crystal chemical complexity. In the second half of the 20th century, it was widely accepted that natural scapolites form a solid-solution series between the two theoretical end-members: $Na_4AI_3Si_9O_{24}Cl$ (marialite) and $Ca_4A1_6Si_6O_{24}CO_3$ (meionite). In 1998, a third end-member of this group of minerals has been approved under the name silvialite ($Ca_4Al_6Si_6O_{24}SO_4$, Teertstra et al., 1999). The interest in such compounds originates mainly from the opportunities for their use as geothermometers, and their potential for greenhouse gas storage. Their crystal structure is composed of a $[(Si,Al)_nO_{2n}]$ framework, containing eight- and four-membered rings. Calcium and sodium cations are located in channels, formed by the eight-membered rings; carbonate, sulphate and chlorine anions occupy channels formed by the four-membered rings (Fig. 1a, b). There are three types of heterovalent isomorphism for group members, generally represented as follows: Si↔Al (framework cations); Ca↔Na and CO_3↔SO_4↔Cl (extra-framework species). Relations between the three schemes are not always explicit and unambiguous, but essentially, their joint manifestation leads to electroneutrality. The highest symmetry space group used in solving crystal structures in the marialite-meyonite series $Na_4Al_3Si_9O_{24}Cl$ (*Me0*) – $Ca_4Al_6Si_6O_{24}CO_3$ (*Me100*), is the tetragonal *I4/m*. It is applicable to the representatives falling within the compositional ranges in the vicinities of the two end-members. In the middle region, however, additional reflections are observed in the diffraction patterns, which require the use of the primitive $P4_2/n$ of the tetragonal syngony. These are (h+k+l) odd reflections forbidden for *I4/m.* Drawing boundaries between the representatives of the two space groups, especially those with high calcium content, is still controversial. The range of the $P4_2/n$ scapolite, as defined by various authors, may comprise group members as follows:

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from (*Me21*) to (*Me77*); from (*Me6*) to (*Me93*), and even from (*Me0*) to (*Me100*) (Sokolova, Hawthorne, 2008; Antao, Hassan, 2011).

In Bulgaria, scapolites occur mainly as rock-forming minerals, less often in pegmatite or sulphide veins mainly in the Sredna Gora and Rhodopes regions (Kostov et al., 2022). There are very few specialized studies devoted predominantly to mineralogical characteristics. Thus, in 1969, S. Petrussenko described scapolites from several localities in Northwestern Rila Mountain (Petrussenko, 1969). Based on classical chemical analysis, he defined the findings as carbonate-sulphate type *mizzonite* (*Me50–80*) with meionite content of 62.6 to 71.7%. In 1979, M. Stojnova described scapolite from the Mladenovo Deposit, Malko Tarnovo District and defined the studied samples as *dipyr* (*Me20–50*) with meionite content varying from 42.42 to 48.14% (Stojnova, 1979). In 2005, D. Stavrakeva and S. Petrusenko reported zonal scapolite from Samurski Dol, Chepelare region, Central Rhodopes. In their study, it is vaguely defined as intermediate scapolite to mariallite based only on the d-spacings of the studied samples and without any chemical analyses applied. The attributions of the examined samples to the mariolite-meionite series are undoubtedly influenced by the limitations of the methods used to determine the meionite content and especially those of the classical (wet) chemistry, which allows the presence of impurity elements/mineral phases in the analyses of such compounds.

Geological setting and previous mineralogical studies on Samurski Dol, Chepelare region

The metamorphic rocks in the Chepelare area have subsequently been exposed to a later action of the Alpine orogen pegmatitic-pneumatolytic activities (Stavrakeva, Petrusenko, 2005). A forsteritic marble quarry is situated in the metamorphic rock formation in the SE part of the region, about 1 km east of the town of Chepelare. The following minerals were discovered in the marble of this area: kyanite (Kostov et al., 1962), sillimanite (Petrussenko, 1968), pink clinozoisite (Petrussenko, Padera, 1970); forsterite, diopside, tremolite, titanite, scapolite (mariallite), anorthite, phlogopite, orthoclase (Stavrakeva, Petrusenko, 2005).

The present study provides new crystallochemical data for the scapolite from Samurski Dol, Chepelare region. Based on energy-dispersive X-ray analyses (EDXA) and single crystal structure determinations (SXDA), a more precise determination of the meionite content than those previously made for this locality has been carried out. The crystal structure of the studied sample has been solved in both $I4/m$ and $P4_2/n$ space groups, traditionally assigned to scapolite members. The aim is to shed more light on the still controversial question for the correct choice of space group in the description of this group's representatives.

Materials and methods

A crystalline sample from the Samurski Dol locality, currently preserved in the National Museum of Natural History at the Bulgarian Academy of Sciences, Sofia under the number 8126 was used for the present studies.

Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS). SEM and EDS analyses were done on a polished, carbon-coated section of a scapolite-containing sample from Samurski Dol locality using X-MaxN 50 mm^2 EDS detector by Oxford Instruments (20 kV accelerating voltage), mounted on a Tescan Vega 3 XMU electron microscope at the Research and Development Department of Aurubis Bulgaria AD, Pirdop. AZtecs Energy software was used for data collection, integration and corrections, using integrated factory standards. Chemical formulae of the studied scapolite have been calculated based on 13 analyses under the following assumptions: (i) Al+Si = 12 apfu (Z=2); (ii) CO_3 = 1–Cl–SO_4; conversion factors S→SO_4(3), Cl→Cl(1); (iii) negligible amounts of detected Mg and K have been referred to Ca^{2+} and Na^+, correspondingly; (iv) *% Me* = Ca*100/(Ca+Na).

Single crystal X-ray diffraction analysis (SXDA). The crystal from the studied compound was mounted on glass capillary and analyzed by a single crystal diffraction method. The data collection and data reduction were performed by CrysAlisPro, Rigaku Oxford Diffraction, 2017, version 1.1.171.37.35 (Agilent, 2010). The diffraction pattern characterizes the studied sample as a single-phase one. The crystal structure was solved by direct methods using ShelxS and refined by the full-matrix least-squares method of F^2 with ShelxL programs (Sheldrick, 2008). All of the atom positions were located successfully from Fourier map. The tetrahedral positions were assumed to be Si/Al mixed with occupancy parameters of Al and Si fixed accordingly to the deviations from the standard Si/Al – O distances. The Ca and Na cations share common crystallographic position and the same is valid for C and Cl anions. The occupancy parameters of Ca, Na, C and Cl atoms were refined with the only constraint being to maintain 100% occupancy of the corresponding anion or cation position. The differences between the theoretical and analytical structural factors were first achieved for the model with isotropic temperature displacement parameters and then for the anisotropic refinement including all of

the atoms. The obtained structural model is optimal with respect to the reliability factors and the chemical analysis data.

Results and discussion

Figure 1c shows part of the mineral association established in the polished section of the studied sample including scapolite, pink clinozoisite, and oligoclase. The scapolite displays traces of alteration (sericitization – Ms) caused by later low-temperature hydrothermal processes.

The chemical composition of unaltered scapolite as determined by EDS and its crystal chemical formula is $(Ca_{2.87–3.00},Na_{1.13–1.00})_4(Al_{4.83–5.00},Si_{7.17–7})_{12}$ $(0.77–0.92CO_3,0.20–0.03SO_4,0.03–0.05Cl)$, *% Me* = 71.75–75. The chemical composition of some of the associated minerals and their crystal chemical formulas are as follows: plagioclase (oligoclase) – $Na_{0.73}K_{0.03}Ca_{0.24}Al_{1.24}Si_{2.76}O_8$, Ca/(Ca+Na) = 25.6% anorthite; pink clinozoisite – $Ca_2(Al_{2.69},Fe_{0.32},Mn_{0.02})_{3.03}[Si_2O_7][SiO_4]O(OH)$; muscovite/sericite – $K_{0.9}Al_{1.9}(Si_{3.2}Al_{0.8})O_{10}(OH)_2$.

According to the prevailing opinion in the previous studies and the value of the determined meionite component, the crystal structure of scapolite from Samurski Dol should be solved in space group $P4_2/n$ (see Introduction). The data in Table 1 show that both groups, used to solve the structure, were equally plausible. In the case of $I4/m$, the reliability factors exhibit better values, but this is most likely due to the data reduction caused by the higher symmetry. It should be noted, however, that the chemical composition of the $P4_2/n$ phase is closer to that obtained from the EDS data analyses. Regarding the framework construction, the two alternatives differ in that the *T2*(Si,Al) tetrahedron ($I4/m$) splits into *T2*(Si,Al) and *T3*(Si,Al) in the $P4_2/n$ case (Fig. 1a,b). Such splitting enables a differentiation of the two derivative tetrahedra by dimensionality. This is related to the preferences of silicon (^{IV}Si–O = 1.61 Å) and aluminum (^{IV}Al–O=1.75 Å) ions to occupy a given position and hence to their arrangement in the framework following or not Lowenstein's rule (Loewenstein, 1954). Larger differences in size are associated with the more intense manifestation of the so-called "forbidden" reflections for the *I*-centered cell of the tetragonal syngony. This is precisely what is observed for the scapolite representatives located in the central range of the marialite-meionite composition series. However, the intensity of these reflections gradually decreases in the direction of the two end-members. Yet there is no sufficiently reliable experimental evidence of their complete absence in these areas. Obviously, approaching the disputed boundaries for the application of a specific space group, the choice largely depends on the vision and understanding of the researcher whether to accept as real or to ignore as low-value the intensities of the so-called "forbidden" reflections.

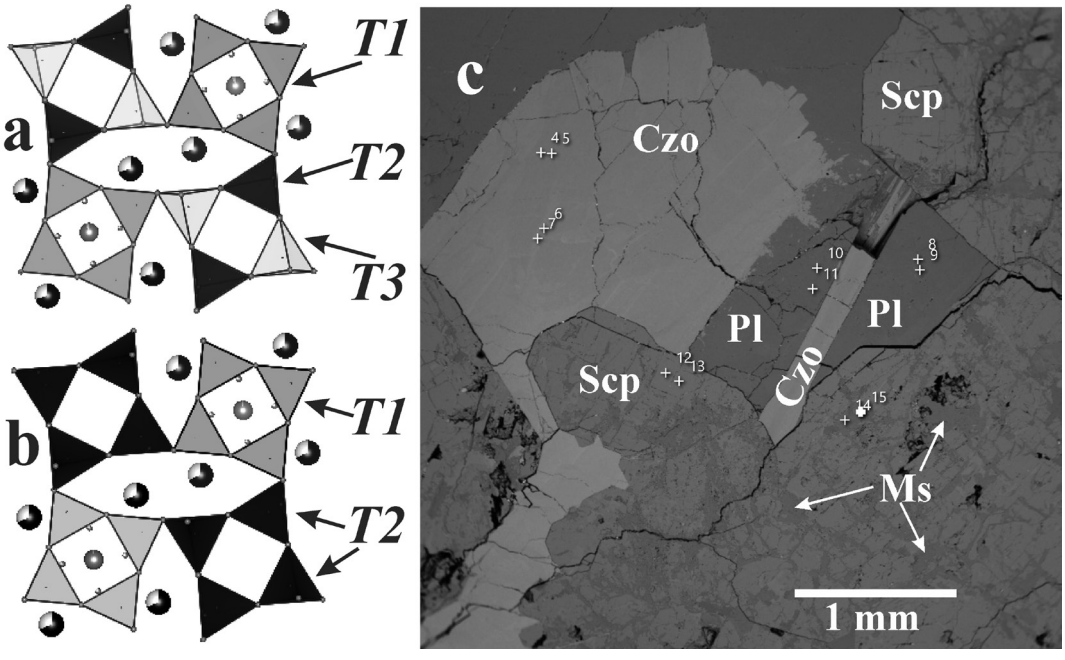

Fig. 1. Crystal structures of a $P4_2/n$ (*a*) and a $I4/m$ (*b*) tetragonal scapolite: *T*n, (Si,Al) tetrahedron; large circles, Ca (black) and Na (white); small circles, C, S, and Cl. SEM image of the mineral association of scapolite (Scp) from Samurski Dol with clinozoisite (Czo) and oligoclase (Pl), and muscovite (Ms) as alteration product (*c*).

Table 1. Crystal data and structure refinement parameters for the scapolite from Samurski Dol locality

Data \ Space group	$P\,4_2/n$	$I\,4/m$
Chemical formula /Z	$Ca_{5.72}Na_{2.28}Al_{9.68}Si_{14.32}O_{53.64}C_{1.88}Cl_{0.12}$ /1	$Ca_{5.49}Na_{2.51}Al_{9.72}Si_{14.28}O_{53.87}C_{1.96}Cl_{0.04}$ /1
Formula weight	1830.16	1827.99
Crystal system	Tetragonal	Tetragonal
a/Å	12.1430(10)	12.1345(6)
b/Å	12.1430(10)	12.1345(6)
c/Å	7.5619(6)	7.5721(7)
Volume/Å^3	1115.0(18)	1114.96(15)
ρ_{calc} (g/cm^3)	2.726	2.722
Crystal size/mm^3	0.02x0.02x0.01	0.02x0.02x0.01
Temperature/K	290K	290K
Radiation, λ [Å]	0.71073	0.71073
Θ range for data collection/°	2.372 to 26.370	2.374 to 26.272
Reflections collected /unique	23904 / 1136[R(int) = 0.0403]	12387 / 610[R(int) = 0.0368]
Completeness to theta = 26.301	99.1%	98.4%
Data/restraints/para-meters	1136 / 0 / 103	610 / 0 / 62
Goodness-of-fit on F^2	1.248	1.124
Final R indexes [I>=2σ (I)]	$R1$ = 0.0348, $wR2$ = 0.1228	$R1$ = 0.0302, $wR2$ = 0.0785
Final R indexes [all data]	$R1$ = 0.0410, $wR2$ = 0.1293	$R1$ = 0.0310, $wR2$ = 0.0789
Largest diff. peak/hole /e Å^{-3}	1.287/-0.543	1.090/–0.578
Selected averaged interatomic distances (Å)	Si1-O – 1.637(1) Si2-O – 1.658(1) Si3-O – 1.692(1) Ca-O – 2.597(1) C-O – 1.303(1)	Si1-O – 1.638(1) Si2-O – 1.675(1) Ca-O – 2.597(1) C-O – 1.297(1)

Conclusion

Based on EDS and SXDA, a more precise determination of the meionite component of a representative of the scapolite group from Samurski Dol, Chepelare region was made. Solving the crystal structure in two possible space groups of the tetragonal syngony shed new light on the choice of space group for description of scapolites crystal structures, as well as on the preferred by silicon and aluminum ions positions and hence for their ordering in the framework construction.

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