

PRELIMINARY DATA ON THE CRYSTAL-CHEMICAL CHARACTERISTICS OF BERYL FROM CER MT. (SERBIA)

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Abstract: A beryl crystal from Cer Mt. (Serbia) studied in this paper was characterized by means of XRPD and wet-chemical analyses. It has following unit cell dimensions: $a = 9.2166(8) \text{ \AA}$, $c = 9.192(1) \text{ \AA}$, $V = 676.2(1) \text{ \AA}^3$ and ratio $c/a = 0.9973$. According to the calculated c/a ratio and structural formula of $(\text{Be}_{2.86}\text{Li}_{0.11})_{2.97}(\text{Al}_{1.96}\text{Fe}^{2+}_{0.05})_{2.01}\text{Si}_{5.96}\text{O}_{18}(\text{Na}_{0.09}\text{Ca}_{0.03}\text{Mg}_{0.03}\text{K}_{0.01})_{0.16} \times 0.14\text{H}_2\text{O}$ composition, this sample belongs to the “normal beryl group”. The obtained characteristics prove that the host pegmatite is of Li-bearing type.

Keywords: Serbia, Cer Mt., Li-pegmatite, crystallography, chemistry, beryl.

1. Introduction

Beryl, with ideal formula of $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, is mainly found as accessory mineral in pegmatites, and it is the most abundant mineral of beryllium in nature. Although a very large number of works have been devoted to investigating members of the beryl group using various methods, these minerals have continued to attract the particular attention of many researchers because of their very complex crystal-chemical behavior and variations of physical properties (see for examples: Aurisicchio et al., 1988; Sheriff et al., 1991; Artioli et al., 1993; Gatta et al., 2006; and references therein).

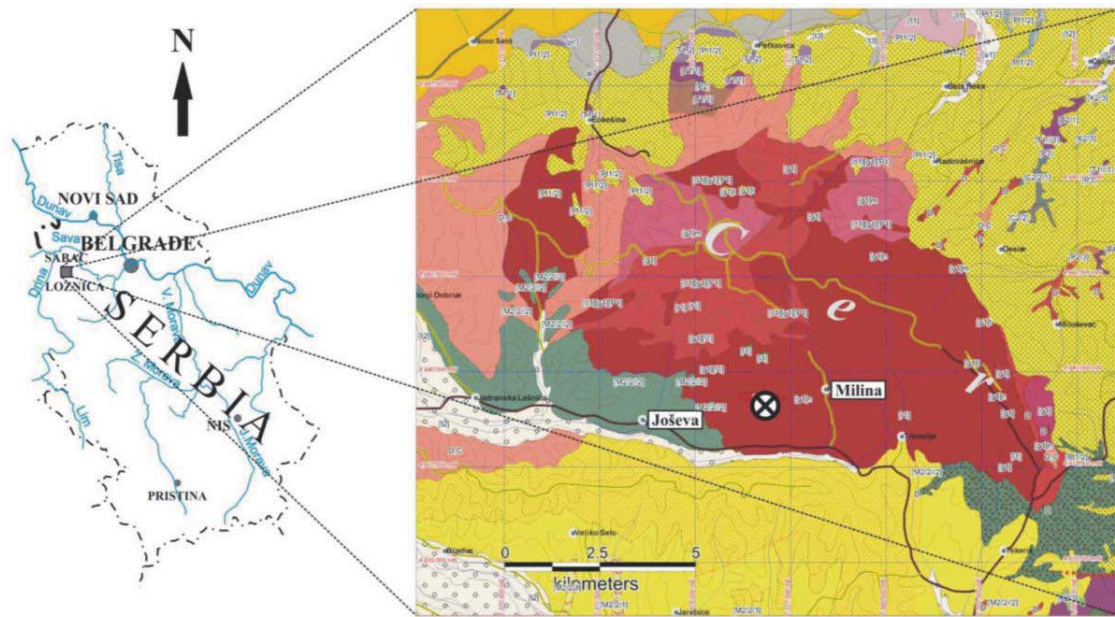
The crystal structure of beryl (space group $P6/mcc$), which was first studied by Bragg and West (1926), consists of isolated six-membered $[\text{Si}_6\text{O}_{18}]^{12-}$ rings perpendicular to the (001) axis. These rings are joined into a single framework structure via AlO_6 octahedrons and BeO_4 tetrahedrons along the c axis of the hexagonal unit cell. The channels formed by the $[\text{Si}_6\text{O}_{18}]$ rings are 2.5-5.0 \AA in diameter, might be filled in with large-sized low-charged cations (Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+}), or molecules such as water and CO_2 , as well as rare gases. The presence of these components in variable amounts and the isomorphism of the framework positions, primarily, octahedral and tetrahedral positions (substitutions of Fe^{2+} , Fe^{3+} , Cr^{3+} , V^{3+} , Mn^{2+} and Mg^{2+} for Al^{3+} ; and Li^+ for Be^{2+}), are responsible for the wide range of beryl composition, sometimes differing significantly

from the ideal formula. Such various substitutions are expressed by a general formula: $(\text{Cs,Rb,K,Na})_{x+y}\text{Al}_{2-x}\text{Me}^{2+}_x\text{Be}_{3-y}\text{Li}_y\text{Si}_6\text{O}_{18} \times z\text{H}_2\text{O}$ ($0 < x+y < 1$; $0 < z < 2-x-y$) (Gatta et al., 2006).

The aim of this paper is to define one natural beryl sample from Cer Mt. by means of its crystallographic and chemical characteristics. Such obtained data was used for comparison with other reference samples. Additional analyses by means of other methods (i.e. FT-IR, Raman, DTA, TGA analysis, structure refinement, etc.) will be further published elsewhere.

2. Geological setting

The granitoid massif of the Cer Mt. is situated in western Serbia, 80 km far from Belgrade, halfway between the towns of Šabac and Loznica (Fig. 1). The massif intruded in Upper Paleozoic (carboniferous) schists (Stevanović, 1951), belonging to the Inner Dinaridic regional structural zone in the NW part of Serbia (Đoković et al., 1997). According to its geological position the main part of the Cer massif is estimated to be of Lower Miocene age. Due to the results of the petrologic investigations (Karamata et al., 1994; Knežević et al., 1994; Knežević et al., 1997), the granite rocks of the Cer massif have been formed by melting of sediment protholites of the continental crust, or by partial melting of earlier granites. It is believed that they were consolidated 14-16 Ma ago.



LEGEND:

d Slope wash sediments	[g1]t Tourmaline granite	[M2/1] Marls, shales and sandstones	D Phyllites and quartz sandstones + contact metamorphic rocks
[t2] Sands and gravels	[g1]n Granite porphyry	[P11/2] Sands, gravels and clays	D Phyllites and quartz sandstones + thermal metamorphic rocks
b Marsh sediments	[G1]m Two-mica granite	[P11/2] Sands and gravels and sandy clays	[g1][f1] Aplitic granites
a Sands and silt sands	[T1,2] Claystones, sandstones and limestones	[r1] Pegmatites	[t1]d Tourmaline granites
[P11/2] Sands, gravels and clays	[d1][g1][P1] Granodiorite	[K2/3] Massive limestones	[g1]n Granite porphyres
M, P1 Sands, gravels, agglomerates and clays	[C2/2] Shales	[T2/1] Dolomites and dolomite limestones	[g1] Two mica granites
am Still water sediments	[C2/2/1] Limestones	[T1/2] Mica sandstones, clayey schists and limestones	[g1]m Two mica granites with muscovite porphyroblasts
[M2/2/2] Marly sandstones	[D3]+C Conglomerate-schist series	[E3] Flysch	[d1][g1][P1] Biotite and biotite-amphibolite granodiorites
[M2/2/2] Sandstones, claystones and marls	D, C Quartz sandstones	[P3] Bituminous limestones	D, C Sandstones and phyllites
[M2/2/1] Sheet limestones	D Quartz sandstones, conglomerates and breccias	[P2/3] Bedding dolomites	Hydrothermally altered rocks, contact-metamorphic rocks?
[M2/2/2] Sandy clays	D Phyllites and quartz sandstones	[I1] Lamprophyre	Sampling point

Fig. 1. Geographical and geological maps of Serbia and wider area of the Cer Mt., respectively, with indicated sampling point location of the investigated beryl.

The Cer massif has a complex petrological composition and forms an irregular lenslike body with a surface area of about 60 km², trending E-W (Urošević, 1899; Knežević, 1962).

Previous investigations have described rocks of the main body as either biotite-hornblende-quartz monzonite or granodiorite. However, some smaller irregular masses in the western part of the granito-

id massif were identified as two-mica granite (Divljan et al. 1978). Granodiorite mass is crosscut by a large number of thin aplitic and pegmatitic veins, the latter younger than the first ones. There are also several small lenticular masses of aplitic granite containing variable amounts of muscovite and biotite as well as sporadically occurring tourmaline and garnet.

There are many indications that the geochemical increase of Li is characteristic for the first stage of metasomatism, whereas the increase of Sn and to a lesser extent of Be, Nb, Ta, Bi and U, took place during the final stages which are characterized by intensive muscovitization and partly by greisenization. Presence of more than 50 mineral species (Divljan et al. 1978; Mudrinić and Stajević 1990), which has been found in the Cer granitoides and their contact aureoles, indicates the complexity of its magmatic and post-magmatic evolution (Urošević, 1899; Nikolić, 1962; Pavlović and Nikolić, 1969; Stanley et al., 2007; Lazić et al., 2009).

The beryl sample addressed in this contribution was found on the southern slopes of the Cer Mt., between Joševa and Milina (Fig. 1). Wider area of this locality is known for the presence of a few large Li-pegmatite bodies. In general, discussed Li-pegmatite bodies containing spodumene represent typical Li-rich pegmatites (Stewart, 1978). One of these is located beside the road to the top of the Cer Mt., and it is used as a quarry. This Li-pegmatite body is characterized by quartz-feldspar-mica-spodumene mineral associations (Pavlović and Nikolić, 1969), with sporadic appearance of garnet, tourmaline, beryl etc. This association indicates an intensive hydrothermal alteration action which transformed spodumene into a mixture of illite and quartz. Another feature of this pegmatite body is the presence of numerous cracks and fissures filled with secondary quartz, Fe-hydroxide and meta-autunite (Lazić et al., 2009).

3. Materials and Methods

A pale greenish-blue beryl mega-crystal found on the south slopes of Cer Mt. (Serbia) was chosen and used for the study. The crystal has *ca* 8 × 8 × 12 cm size and volume of *ca* 750 cm³ (Fig. 2). One part of the sample was cut down, powdered under alcohol in agate mortar, and further examined with the X-ray powder diffraction (XRPD) and chemical methods.

The XRPD pattern was obtained with a Philips



Fig. 2. The pale greenish-blue beryl mega-crystal subjected for the study.

PW-1710 diffractometer using a Cu tube operating at 40 kV and 30 mA. The instrument was equipped with a curved graphite monochromator and a Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angle range from 4° to 90°, counting for 1.5 seconds at every 0.02° steps. The divergence and receiving slits were fixed at 1° and 0.1 mm, respectively. The XRPD measurements were performed *ex situ* at room temperature in a stationary sample holder. The alignment of the diffractometer was checked by means of a standard Si powder material. Calculation of the unit cell dimensions was accomplished with the LSUCRI program (Garvey, 1987) adapted for the personal computer.

Chemical analysis was performed on the sample decomposed with Na₂CO₃ and Na₂B₄O₇ (2:1) at the temperature of 1000 °C and also by combination of HClO₄ and HF (2:1) acids, worming to dryness. Afterward, most of the elements were determined by atomic absorption spectrometry (AAS, Perkin-Elmer 6500). The SiO₂ component was determined by the gravimetric method; whereas the Fe²⁺ component was determined with the permanganometry method after decomposition with mixture of diluted H₂SO₄ and HF acids in an inert atmosphere to avoid its oxidation.

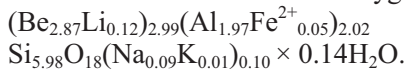
4. Results and Discussion

The X-ray diffraction pattern obtained for pow-

dered beryl sample is displayed in Fig. 3. The values of the observed inter-planar spacings of this pattern indicate that the investigated sample is of very high purity, i.e. consisting of only beryl.

Based on the 48 reflections corresponding to the $P6/mcc$ space group (Bragg and West 1926), the unit cell dimensions of beryl were calculated as: $a = 9.2166(8) \text{ \AA}$, $c = 9.192(1) \text{ \AA}$, $V = 676.2(1) \text{ \AA}^3$ and ratio $c/a = 0.9973$.

The obtained chemical analysis of the investigated sample (*i*) is listed in table 1. It should be mentioned that about 1-1.5 % of the sample still remained un-dissolute by unknown reasons. Therefore, this analysis was first normalized to 100 % (*ii*), and after that following structural formula was calculated at basis of 18 oxygen a.p.f.u. (*iii*):



Due that substitutions of Fe^{2+} for Al^{3+} and Li^+ for Be^{2+} exceed total content of Na and K (i.e. 0.17 vs.

0.10; left *iii* columns in Tab. 1), it should be taken into account that the structural channels are also occupied with Ca and Mg cations, as Hawthorne and Černý (1977) supposed. At such way, $(\text{Be}_{2.86}\text{Li}_{0.11})_{2.97}(\text{Al}_{1.96}\text{Fe}^{2+}_{0.05})_{2.01}\text{Si}_{5.96}\text{O}_{18}(\text{Na}_{0.09}\text{Ca}_{0.03}\text{Mg}_{0.03}\text{K}_{0.01})_{0.16} \times 0.14\text{H}_2\text{O}$ formula is obtained. Now, the substitutions of Fe^{2+} for Al^{3+} and Li^+ for Be^{2+} are equal to the cation occupation in the channels (i.e. 0.16 vs. 0.16; right *iii* columns in Tab. 1), and it seems to be more appropriate.

Bakakin et al. (1970) and Aurisicchio et al. (1988) demonstrated the existence of two important kinds of substitution in beryl, giving rise to two distinct solid-solution series. These are “tetrahedral” beryl in which the dominant substitution is of Li^+ for Be^{2+} on the distorted tetrahedral site, and “octahedral” beryl in which the dominant substitution is of Fe^{2+} and Mg^{2+} for Al^{3+} on the octahedral site. In both cases charge balance is maintained by alkali ions entering channel sites. The two series may be distinguished by their c/a ratio which is 0.991-

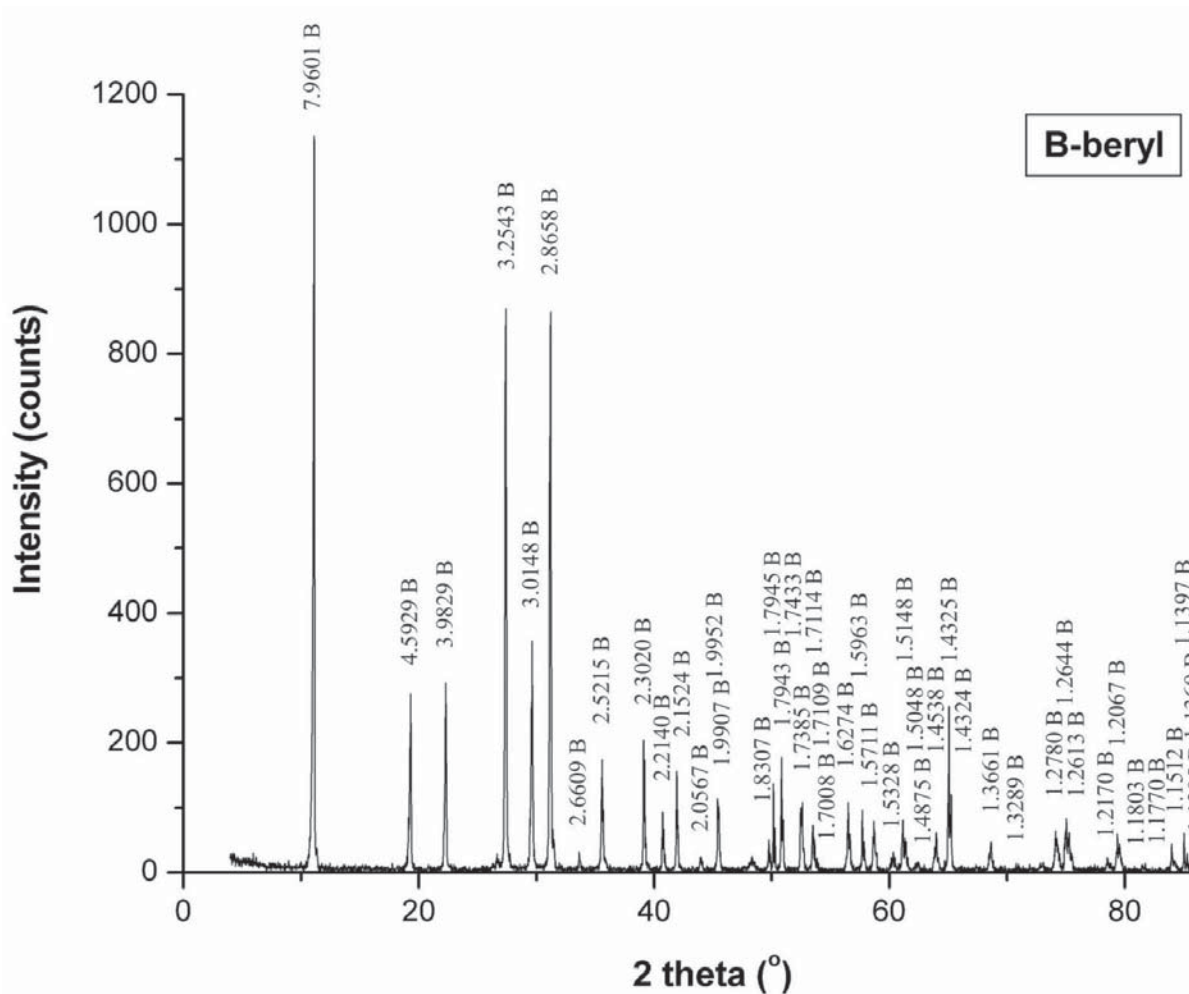


Fig. 3. X-ray powder diffraction pattern of the investigated beryl sample.

Table 1. Obtained chemical composition (marked as “*i*”; in wt. %), normalized chemical compositions to 100 % (marked as “*ii*”; in wt. %), and structural formulas normalized to 18 oxygen a.p.f.u. (marked as “*iii*”).

Oxide	<i>i</i>	<i>ii</i>	<i>iii</i>	<i>ii</i>	<i>iii</i>
SiO ₂	65.11	66.35	5.98	5.98	5.96
TiO ₂	n. d.	n. c.	n. c.	n. c.	n. c.
Al ₂ O ₃	18.19	18.54	1.97		1.96
Cr ₂ O ₃	n. d.	n. c.	n. c.	2.02	n. c.
Fe ₂ O ₃	n. d.	n. c.	n. c.		n. c.
FeO	0.64	0.65	0.05		0.05
MnO	n. d.	n. c.	n. c.	n. c.	n. c.
CaO	0.32	n. c.	n. c.	n. c.	0.03
MgO	0.19	n. c.	n. c.	n. c.	0.03
Na ₂ O	0.48	0.49	0.09		0.09
K ₂ O	0.12	0.12	0.01	0.10	0.01
Cs ₂ O	0.03	0.03	0.00		0.00
Rb ₂ O	0.01	0.01	0.00		0.00
BeO	13.02	13.27	2.87		2.86
Li ₂ O	0.30	0.31	0.12	2.99	0.11
H ₂ O ^{1000C}	0.23	0.23	0.14	0.14	0.14
H ₂ O ^{110C}	0.07	n. c.	n. c.	n. c.	n. c.
Σ	98.71	100.00	18 O	18 O	18 O

n. d. – not detected, n. c. – not calculated

0.996 for “octahedral”, and 0.999-1.003 for “tetrahedral” beryls. The “normal” beryls with *c/a* ratios between 0.997 and 0.998 include those where the two substitutions occur together, though to a limited extent.

According to this definition, and at basis on the calculated *c/a* ratio of 0.9973, the investigated sample belongs to the “normal beryl group”. Also, its other crystallographic characteristics (i.e. intensities, inter-planar spacings and unit cell dimensions), could preliminary indicate that it is quite similar to the samples investigated by Gibbs et al. (1968), Morosin (1972), Sheriff et al. (1991), Artioli et al. (1993) and Gatta et al. (2006), as well as some particular samples determined by Aurisicchio et al. (1988).

On the other hand, determined chemical composition and structural formulas (Tab. 1) narrower such crystallographic sample similarities, indicating that it is quite different to the most of the previously mentioned samples and similar only to a few specimens summarized by Aurisicchio et al. (1988; Tabs. 2-3; and diagrams presented at Figs. 5-8). Furthermore, a limited extent of the two substitutions in octahedral and tetrahedral positions (i.e. substitutions of about 2 % of Fe²⁺ for Al³⁺; and of about 4 % of Li⁺ for Be²⁺), is also confirmed.

An approximate ratio of 2:1 of H₂O to Na has been previously noted (Hawthorne and Černý, 1977; Sanders and Doff, 1991). That suggests that most, if not all the Na in investigated beryl is bonded to

two water molecules (Type II water). But, due that such problematic is beyond the scope of this paper, it will be further investigated with other methods.

The scheme given by Černý (1975) indicated that the alkali content of beryl may be used quantitatively to further delineate the geochemical characterization of pegmatites and to identify petrogenetically related pegmatite groups. Accordingly, at basis of the chemical analysis (Tab. 1) the investigated sample in present paper belongs to the sodic-lithian beryl (i.e. Na ranges between 0.0-2.0 wt. %; Li up to 0.6 wt. %; Cs low; occurs in Li-bearing pegmatites), further approving that the host pegmatite is of Li-bearing type.

5. Conclusion

A beryl sample related to pegmatitic veins cross-cutting the granitoid massif of the Cer Mt. (Serbia) was investigated by means of XRD and wet-chemical analyses. The obtained data point to the presence of a so-called “normal beryl type” and indicate a Li-bearing type of the host pegmatite.

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