Raman spectra, morphology and color of beryl

Раманови спектри, морфология и цвят на берил

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Introduction

It is well known that beryl is cyclosilicate mineral ($Be_3Al_2Si_6O_{18}$) with a structure consisting of 6-membered rings (Si_60_{18}) and cell data: *P*6/*mcc, a* = 9.208 Å, *c* = 9.175Å. The channels in the structure are most commonly occupied by cations such as Na^+, K^+, Li^+, Cs^+, as well as by water and CO_2 or some combination of the above (Gaines et al.,1997). It is widely accepted (Gaft et al., 2005) that heliodor color is a result of Fe^{3+} substituting for either Be^{2+} or Al^{3+}, while variety of color centers in aquamarine is attributed to Fe^{2+} and Fe^{3+}, in addition to traces of color-inducing Mn^{2+} in morganite and Cr^{3+} in emerald. Morphology, color variations and Raman spectra of natural and synthetic beryl crystals (Fig. 1) have been studied here taking into account recently published data.

Results and conclusions

Most of the examined crystals display basal pinacoid {0001}, hexagonal prism $\{10\bar{1}0\}$ and hexagonal bipyramid $\{10\bar{1}1\}$, but other faces as $\{11\bar{2}1\}$, $\{21\bar{3}0\}$ and occasionally dihexagonal prism $\{32\bar{5}0\}$ also appear. In aquamarine crystal (Fig.1a) very rare dihexagonal bipyramid $\{19.1.\overline{20}.1\}$ was measured. Model images of the crystals were drawn by means of VESTA 3D visualization software (Momma, Izumi, 2010) introducing cell parameters, space group and the Miller indices of the measured forms (Fig. 2).

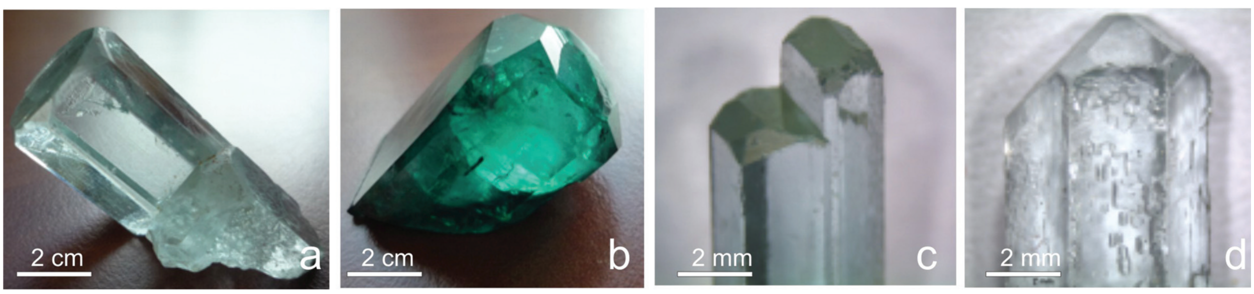

Fig. 1. Photographs of selected beryl crystals: *a*, aquamarine; *b*, synthetic emerald; *c*, aquamarine, Dassu, Pakistan; *d*, aquamarine, Goyongo, Congo

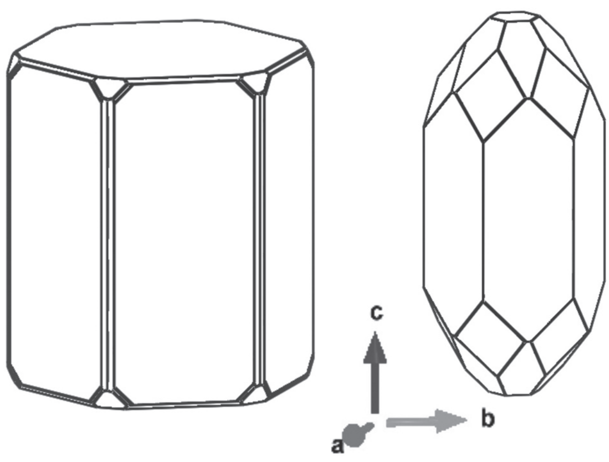

Fig. 2. Morphology of beryl crystals

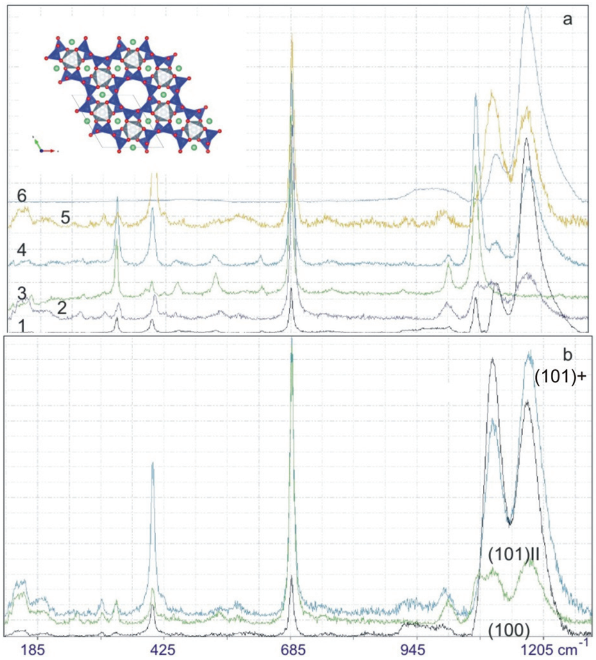

Fig. 3. Unpolarized Raman spectra of beryl varieties recorded in back-scattering geometry on Micro-Raman Spectrometer LabRAM HR Visible (HORIBA Jobin Yvon), 633 nm, He-Ne laser, 7.3 mW: *a*, on (0001) – *1*, aquamarine; *2*, goshenite; *3*, heliodor; *4*, beryl; *5*, morganite; *6*, synthetic emerald; *b*, goshenite in different orientations

Table 1. Observed Raman-active vibrational frequencies (in cm^{-1}) and some assignments of beryl

Vibrational modes		Observed frequencies		Assignments
		present work	Kim et al., 1995	
E_{1g}		146	146	ring rotation
E_{1g}		255	255	
	A_{1g}	323	323	ring breathig
	A_{1g}	396	396	
E_{1g}		450	450	
E_{1g}		529	529	
	A_{1g}	625	625	
E_{1g}	A_{1g}	685	685	
E_{1g}		770	771	Al & internal ring
E_{1g}		919	919	Be & internal ring
E_{1g}		1013	1014	internal ring & Be
E_{1g}		1070	1070	Be & internal ring
	A_{1g}	1105 (br)	1139	combination or overtone
	A_{1g}	1175 (br)	1192	

(br) denotes a broad peak.

Raman spectra of synthetic emerald collected with a 633 nm laser exhibit fluorescence that overwhelms the Raman signal (Fig. 3a) that is due to the Cr^{3+} content. In natural beryl of any other color with low Cr^{3+} as compared with emerald, fluorescence is minimized (Jasinevicius, 2009) as in our case (Fig. 3). In spite of Raman peaks orientational dependence (Fig. 3b) beryl can be reliably identified by Raman spectroscopy.

The observed peak at 323 cm^{-1} (Fig. 3a, Table 1) best matches the beryl Si_6O_{18} ring breathing mode (Kim et al., 1995). Colorless beryl, goshenite has low concentrations of color-inducing atoms such as Cr and V (Gaft et al., 2005) as compared to colored beryl that possibly could explain in our case (Fig. 3) the low intensity peak at 323 cm^{-1}.

Metal ions, charge transfer and color centers seem to be most important factors causing variation in hues, tones and saturations of gem beryl (Fritsch, Rossman,1987) and most probably they affect the Raman spectra at about 200 cm^{-1} and in the range 1070–1200 cm^{-1} (Fig. 3).

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