Luminescence of burbankite-group minerals from carbonatites

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The luminescence research method is successfully used for revealing special features of minerals that either can be used as sufficiently reliable diagnostic indicators or are typomorphic for specific geological environments and mineral formation conditions (Marfunin, 1979). Moreover, luminescence is an efficient tool to detect mineral-indicators of various types of mineralization (zircon, apatite, fluorite, scheelite, diamond), which are rare in rocks and ores but possess characteristic glow.

Burbankite-group minerals are hexagonal and monoclinic (pseudohexagonal) anhydrous carbonates with the general formula $A_{3\div4}B_{3\div2}(CO_3)_5$, where the A site is predominantly occupied by Na and Ca atoms whereas the larger and higher coordinated B site contains a high number of other alkaline earth elements (Ca, Ba) as well as rare earth elements (Belotivtskaya and Pekov, 2004; Hazen et al., 2013).

Below we report the results of a study of laser-induced photoluminescence (PL) of hexagonal members of the burbankite group (strictly burbankite, in which Sr prevails, calcioburbankite, and barium member khanneshite). Investigations were conducted on carbonatite samples from alkaline-ultrabasic complexes of the Kola region (Vuori-Yarvi, Kovdor, Khibina), Yakutia (Ozernyi), Greenland (Qaquarssuk), and Afghanistan (Khanneshin). Carbonatites belonged to different mineral types: calcite (±dolomite), dolomite (±calcite), calcite- and dolomite-ankerite, shortite. The identification of the studied minerals was carried out by X-ray diffraction method and/or electron probe micro-analysis.

The study of the above-mentioned minerals consisted first of a visual evaluation of the luminescence colour and measurements of the spectra of optically active centres related to rare earth elements. The equipment used – microscope-spectrophotometer, nitrogen laser with $\lambda_{exc} = 337.1$ nm, and a computer-based registration system and blocks in line with the CAMAC standard – made it possible to record the spectral-kinetic characteristics of ≥ 20 μm-sized objects in the spectral range 380–850 nm.

Luminescence decay times of different rare-earth luminogens vary appreciably (for example, $\sim10^{-7}$ s for Ce^{3+}, $\sim0.7\times10^{-6}$ s for Eu^{2+}, $\sim1.2\times10^{-4}$ s for Dy^{3+}, and $\sim1.5\times10^{-3}$ s for Sm^{3+}), so we cannot fully register their entire luminescence properties. The "photon counting" method makes it possible to effectively fix the PL of Sm^{3+} and Dy^{3+} (as well as Mn^{2+}), whose decay time is in excess of 10^{-6} s.

Burbankite, calcioburbankite, and khanneshite show intense laser-induced violet luminescence. Note that the colour of the visually observed PL does not depend on minerals own colouring, which varied from colourless to brown. Thus, their colour and luminescence centres are distinguished most probably from each other.

The dominant bands of Sm^{3+} in spectra of all three minerals form invariable combination with maxima at 563–565 nm (I), 598–601 nm (II), 642–647 nm (III), and 702–708 nm (IV), which are caused by optical transitions $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$, and $^4G_{11/2}$ (Fig. 1). The initiation of optically active centers of Sm^{3+} may be caused by an isomorphic Na contamination compensating for the REE excessive positive charge. Previously, this combination of four Sm^{3+} bands was detected through cathodoluminescence in strontianite (Mariano, 1989). Note that some spectra contain Dy^{3+} bands, out of which the most clear-cut one is the 480 nm band. Figure 2 shows the superposition spectrum of Ce^{3+} and Eu^{2+} bands characterized by a short decay time.

The obtained results suggest that hexagonal minerals of burbankite group enriched with lanthanides ($REE_2O_3 \geq 9.5$ wt.%) have violet luminescence, and their PL spectra always contain four Sm^{3+} bands with stable ratios of band intensities, with II > III > I > IV. These characteristics may be used not only as diagnostic but also typomorphic features of burbankite, calcioburbankite, and khanneshite, which often accompany the industrially important mineral-concentrators of the rare earth (bastnäsite, parisite, monazite, in which the content of REE_2O_3 reaches 60-75 wt. %). Therefore it is reasonable to consider luminescent properties of the studied minerals as indicators of potential rare-earth mineralization in the carbonatite-bearing alkaline-ultrabasic complexes.

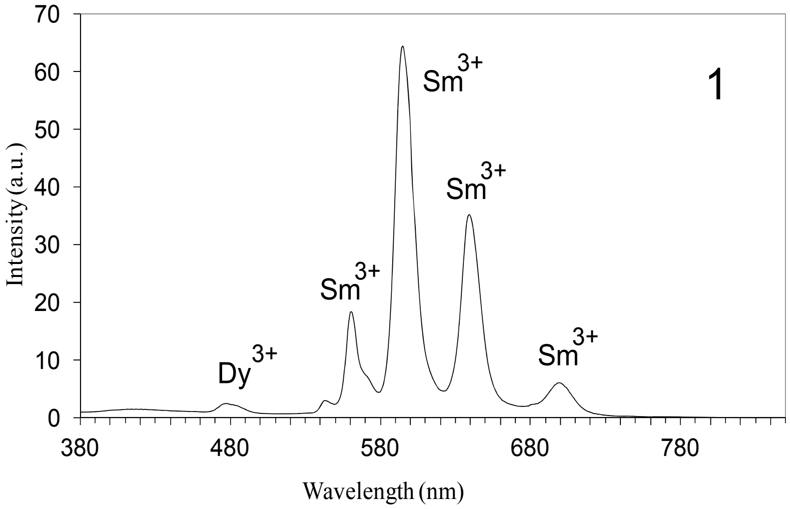

Fig. 1. *Typical photoluminescence spectrum of burbankite from carbonatites.*

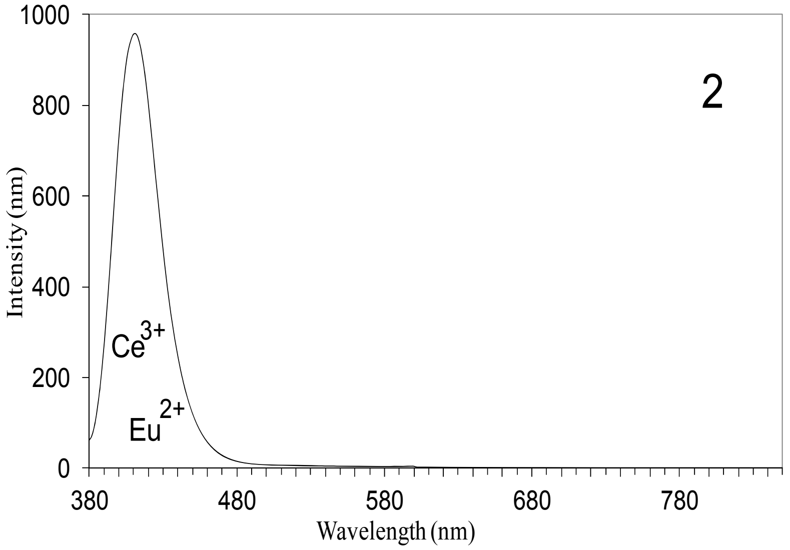

Fig. 2. *Emission spectrum showing the superposition of* Ce^{3+} *and* Eu^{2+} *bands with short decay times (burbankite from carbonatites).*

References:

Belotivtskaya YV, Pekov IV (2004) Genetic mineralogy of burbankite group. New data on minerals 39:50–64

Hazen RM, Downs RT, Jones AP, Kah L (2013) Carbon mineralogy and crystal chemistry. In: Carbon in Earth (Hazen RM, Jones AP, Baross JA, Eds.). Rev Mineral Geochem 75, p 7–46

Marfunin AS (1979) Spectroscopy, luminescence and radiation centres in minerals. Springer, Berlin, 352 p

Mariano AN (1989) Cathodoluminescence emission spectra of rare earth element activators in minerals. In: Geochemistry and mineralogy of rare earth elements (Lipin BR, McKay GA, Eds.). Rev Mineral 21, p 339–348