

IMPURITIES AND COLOR ENHANCEMENT IN TOURMALINE FROM PARAÍBA, BRAZIL

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RESUMO: Vivid blue and bluish-green tourmalines containing copper and manganese as trace elements are one of the most highly-prized gemstones in the market. Discovered in the end of the 1980s in the state of Paraíba, Brazil, they are rare and small. Scientifically, these tourmalines belong to the elbaite family, a sodium-lithium-aluminum-borosilicate with chemical formula $\text{Na}(\text{Li},\text{Al})_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4$ and trigonal space group $R\bar{3}m$ and $Z=3$. Natural samples including a blue, a bluish-green and a bi-colored tourmaline with a pink core and blue rim were investigated by electron microprobe analysis (EMA), Raman scattering, optical absorption, photoluminescence and electron paramagnetic resonance (EPR). Color enhancement processes were also studied using heat under oxidizing and reducing atmospheres in the temperature range from 150°C to 750°C. The chemical analysis of the different samples revealed 1.4 wt. % of Cu in the blue region, whereas in the bluish green and pink part only 0.6 wt. % was detected. In all samples the Mn content is about 0.6 wt. % in addition to 0.3 wt. % of Fe in the bluish-green one. EPR spectra show the presence of high concentration of Cu^{2+} [1] and low concentration of Fe^{3+} in all blue and bluish-green samples. The EPR angular dependencies are consistent with Cu^{2+} in distorted Y-sites of the tourmaline structure. The optical absorption spectra show intense absorption in the near UV and in the visible spectral range centered at about 695 nm. The latter together with a band at 920 nm were attributed to Cu^{2+} [2, 3]. An absorption band earlier found at 515 nm and attributed to Mn^{3+} was missing in the blue and bluish-green samples. Heating experiments on the bluish-green sample in both oxidizing and reducing atmospheres does not affect the Cu^{2+} -related absorption at 695 nm, however, reduce the intensity of the absorption band, which was attributed to Mn^{3+} . We suggest that the bluish-green colors originate from the superposition of the absorption band at 695 nm (Cu^{2+}) and an absorption in the near UV region, which we attribute to $\text{Fe}^{3+} - \text{O}$ transition. [1] R.I. Mashkovtsev, S.Z. Smirnov and J.E. Shigley (2006) *Journal of Structural Chemistry* 47, 252-257. [2] G.R. Rossman, E. Fritsch and J.E. Shigley (1991) *American Mineralogist* 76, 1479-1484. [3] M.N. Taran, A.S. Lebedev and A.N. Platonov (1993) *Physics and Chemistry of Minerals* 20, 209-220. Acknowledgements: We are grateful to FAPEMIG, CNPq and FINEP.

PALAVRAS-CHAVE: TOURMALINE; COLOR; IMPURITY.