High-Frequency and -Field EPR of Natural and Beryllium-Treated Sapphires

A. Somdee, S. Meejoo (Mahidol U., Bangkok, Thailand, Chemistry); J. Krzystek (NHMFL)

Introduction

Gemstones are an important sector of Thailand's economy. Only a small fraction of natural stones, such as sapphires, are of desired color and quality, hence high value. Therefore, obtaining the most desired characteristics in gemstones is of importance for the industry. Various heat treatments can be applied to natural stones in order to change their original colors to highly desired ones and one of the most recent techniques is treatment with beryllium compounds at high temperatures. The nature of the occurring processes is still under debate; among them beryllium diffusion into the corundum lattice has been proposed.

Experimental

Natural blue sapphires were mixed with BeO powder and heated at 1700 °C for 48 hours in an O_2 atmosphere. After that treatment, the natural blue sapphires become a mixture of yellow sapphires and a fraction of light-blue sapphires. Various analytical techniques were employed to investigate the resulting samples, among them LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectroscopy), Mössbauer spectroscopy, and X-band EPR. The NHMFL EMR Facility with its 17-T superconducting magnet was used to detect and characterize the transition metal ions that impart sapphires their color and other properties. HFEPR was used because of its superior resolution compared to X-band EPR in studying transition metal ions such as Fe^{3+}, Cr^{3+}, or Cu^{2+}, and a potential capability of detecting 'EPR-silent' species such as Fe^{2+}.

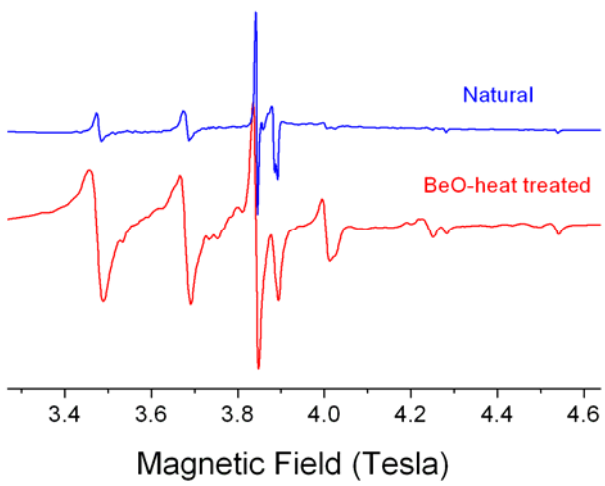

Figure 1. 108 GHz EPR spectra of a natural blue (top) and BeO-heat treated (bottom) sapphire ground into powder, at T = 5 K. Sample amount was the same in both spectra (280 mg). The spectra are dominated by high-spin Fe^{3+} resonances.

Results and Discussion

LA-ICP-MS results delivered no convincing evidence of beryllium lattice diffusion, as no significant amount of beryllium was found in the BeO-heat treated sapphires. At the same time HFEPR indicated a substantial increase of Fe^{3+} concentration in the BeO-treated samples in comparison with natural stones (see Fig. 1). Additionally, UV-Vis absorption spectra of the sapphire samples have shown that natural blue sapphire contains Fe^{3+} and Fe^{2+} but the BeO-heat treated sapphire contains only Fe^{3+}. Neither Mössbauer spectroscopy nor HFEPR succeeded to detect Fe^{2+} in either kind of samples, probably due to its small concentration.

Conclusions

With an excellent agreement between UV-Vis and EPR spectroscopy, it can be concluded that during beryllium heat treatment, Fe^{2+} in blue sapphire converts to Fe^{3+} resulting in no detection of Fe^{2+} by UV-vis spectroscopy and in a detection of a Fe^{3+} content increase by HFEPR for BeO-heat treated sapphires.

Acknowledgements

AS and SM are thankful for the financial support from National Council of Thailand and Center for Innovation in Chemistry-Postgraduate Education and Research in Chemistry (PERCH-CIC) Program. JK was supported by the NHMFL.