Possibility of Identifying Treated and Non-treated Sri Lankan Ruby and Sapphires by FT-IR Spectroscopy

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1. Introduction

Pure corundum is a colourless crystalline form of Al_2O_3. However, the corundum gem family displays different colour formation such as those in Ruby and Sapphires due to chromorphous impurity elements and lattice defects. Among these valuable corundum gemstones, a type of corundum stone with less colour and clarity is also unearthed from the gem pits. These stones are known as 'Geuda' and their quality could be enhanced to the same level of fine gemstones like Ruby and Sapphires by heat treatment.

Heat treatment of corundum gemstones is a common practice and presently, heat treated Rubies and Sapphires are frequently seen in any gem market around the globe. However, there is no global accepted standard stating specifically how a seller should disclose gem treatments, but the recognition of the treatment method when purchasing a gemstone is a very significant factor for the gem buyer or end-user. Therefore, the Laboratory Manual Harmonization Committee (LMHC) has been trying to standardize gem testing. In order to issue a certificate stating the treatment method, a scientific identification regards the method is vital. Traditionally, detailed internal features of Ruby and Sapphires are observed for the identification of heated stones (Kitawakai, 2006). However, the detection of low temperature treated gemstones based on the traditional method has some inherent difficulties (Scarratt, 2006).

In recent times, gemologists have successfully used infrared absorption spectrum to distinguish between heat treated Rubies and Sapphires of metamorphic origin from natural stones. Likewise, the National Gem & Jewellery Authority of Sri Lanka (NGJA) is planning to implement this method to identify the heat treatment status of corundum gemstones and to mention the treatment status in their gemological certificate. It would be consoling news for Sri Lankan and foreign gem buyers who wish to buy world famous Sri Lankan Sapphires. Unfortunately, literature on infrared spectrum of heated and natural Sri Lankan corundum gemstones is still limited.

Therefore, the objective of this article is to acquaint the Sri Lankan gem trade on the application of infrared spectrum for distinguishing treated and non-treated Ruby and Sapphires through Fourier-Transform Infrared Spectroscopy (FTIR).

2. Technology of infrared spectroscopy

2.1.Infrared Energy in Electromagnetic Spectrum

In the electromagnetic spectrum, energy of the space is a sequence from higher energy of cosmic rays to lower energy of radio waves (Fig. 1). Different energy photons (levels) of the spectrum are involved with different changes in gemstones. For instance, the visible range of the spectrum is involved in electron transition in the gemstones and subsequently gives characteristic colours to the stones. The infrared region of the electromagnetic spectrum is the energy range just beyond the red end of visible region (Fig. 1).

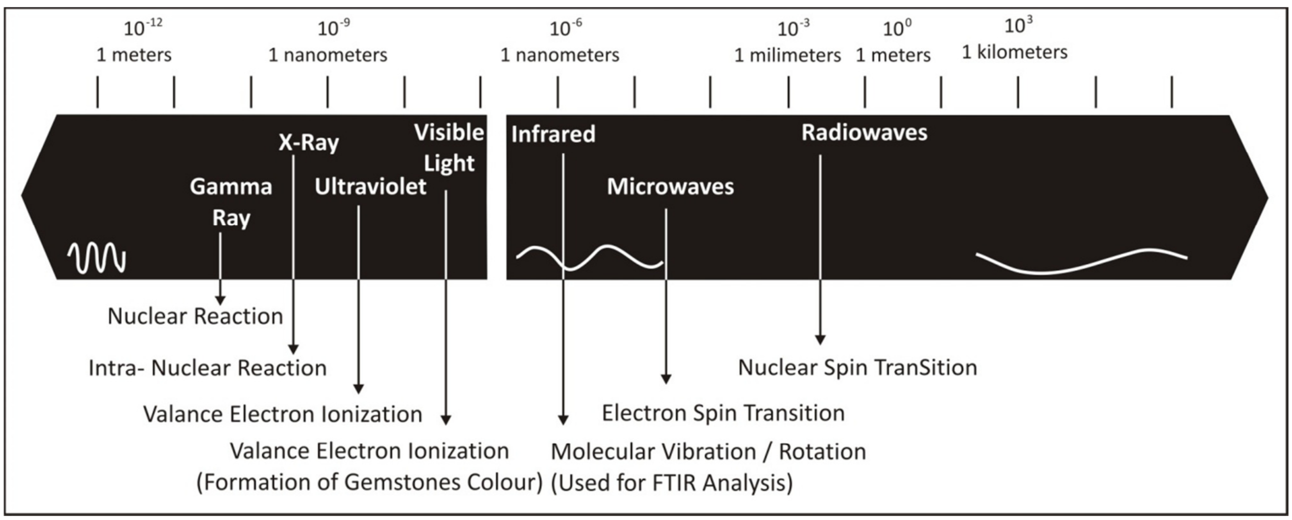

Fig. 1. Electromagnetic spectrum with different changes in gemstones.

Gemstones consist of atoms held together by chemical bonds and they are not composed of stationary elementary particles (i.e. atoms). They are in constant movement (Fig. 2). This phenomenon can be described by a system of springs connecting to the balls in such a way that the springs represent chemical bonds while balls represent atoms. The movement of each ball toward or away from the other ball along the line of the spring represents a stretching vibration (Fig. 2A). Stretching can either be symmetric or asymmetric. A molecule with three or more atoms can experience a bending vibration, a vibrational mode where the angle between atoms changes (Fig. 2B).

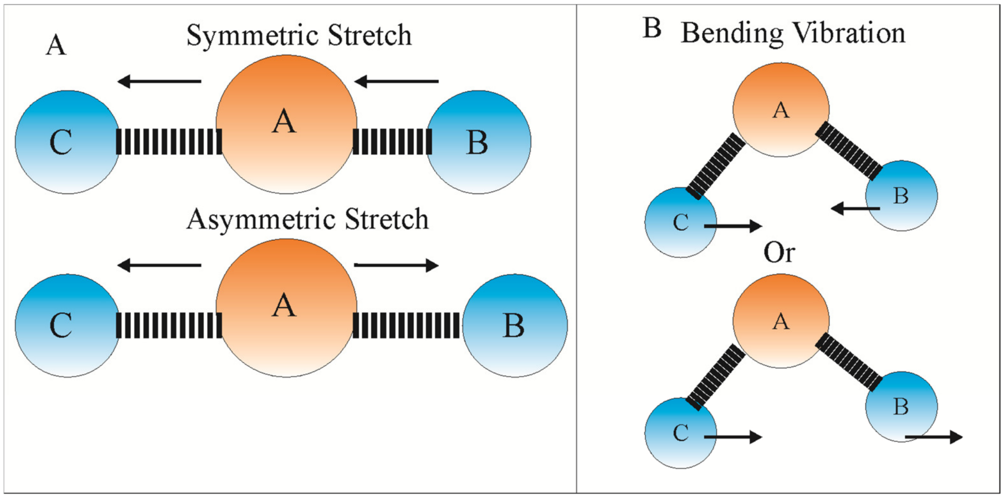

Fig. 2. The movement types associated with bonds

The bond movement has a ground state and an excited state. A particular energy photon is required to transfer a bond motion from ground state to excited state. These energies all lie within the infrared region of the electromagnetic spectrum. Therefore, an infrared spectrum inevitably represents a fingerprint of a gemstone with specific absorption peaks which correspond to the existing bonds of gemstones. Different gem types give characteristic infrared spectrums. Two piece of a gemstone can give one infrared spectrum because of unique combination of atoms. Therefore, this method is applied for the identification of gemstones and can effectively disclose different treatment methods applied to the stone.

2.2.FT-IR Spectrophotometer

Normally, absorption spectrum of infrared region is obtained by FT-IR Spectrophotometer (Fig. 3A). In this sophisticated instrument, infrared energy is passed through the gemstone. Some of the energy levels of the infrared are absorbed by existing bonds and the rest is transmitted within the stone (Fig. 3B). Then, existing bonds of the gemstone were determined considering corresponding infrared absorption energy levels. Subsequently, gemstone type and treatment method was identified.

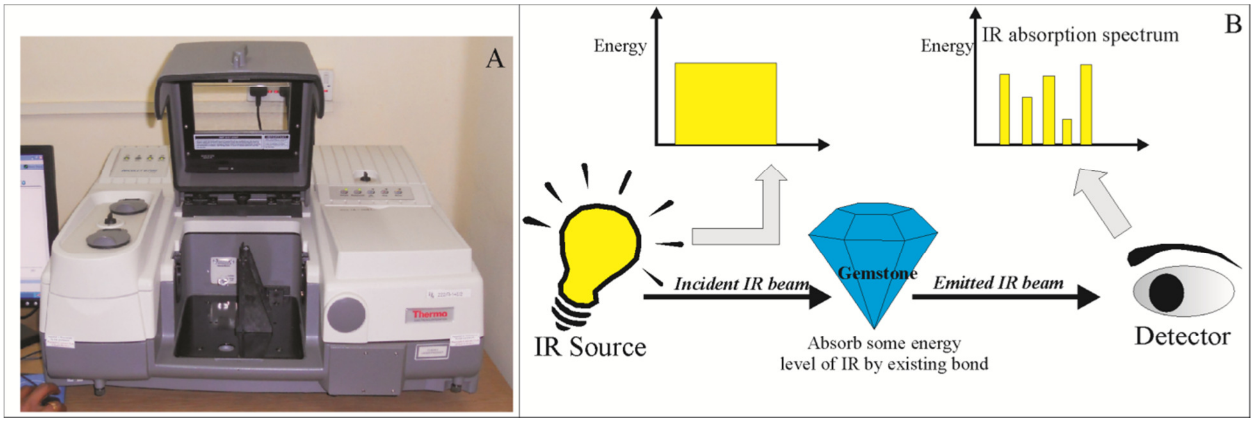

Fig.03. FTIR Spectrophotometer (A) and FTIR working technology (B)

3. Analysis of Ruby and Sapphires by FT-IR method

Mainly, hydroxyl (OH^-) bond stretching peaks were used for the identification of heat treated Rubies and Sapphires. These peaks are situated from 3100 to 3600 cm^{-1}. Beran and Rossman (2006) discovered existing OH stretching IR peaks in the Sri Lankan natural Rubies and Sapphires. Some, Sri Lankan natural Rubies as well as yellow and pink Sapphires displayed OH stretching IR absorption peak at 3160 cm^{-1} (Fig. 4). Natural, metamorphic origin blue Sapphires gave no peak at 3310 cm^{-1}. However, the blue Sapphires unearthed at the Kataragama blue Sapphire occurrence, which presumably originated by pegmatitic intrusion (Dharmaratne et al., 2012) gave a peak at 3310 cm^{-1} (Pardieu et al., 2012). Likewise, heated blue Sapphires also gave characteristic peaks at 3310 cm^{-1}. Therefore, before implementing this method in order to distinguish heated blue and non-heated Sapphire in Sri Lanka, a detail FT-IR analysis on natural and heat treated blue Sapphires is recommended.

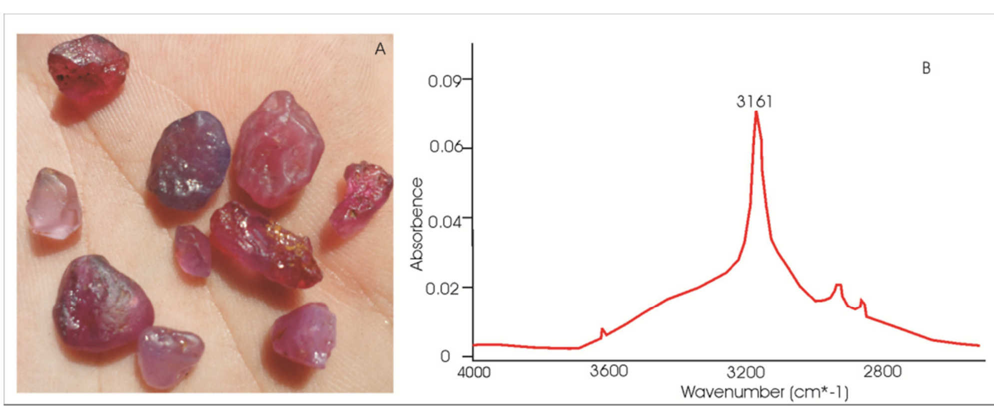

Fig. 4. Pink sapphire and infrared absorption spectrum.

In recent years, one of the most problematic corundum gemstone treatment methods was revealed by Leelawatanasuk et al., 2013 and Christopher, 2013. Lead glass filling treatment started from Ruby and subsequently was extended to other Sapphires, for instance, blue Sapphire and green Sapphire. However, gemmologists have introduced different techniques in order to identify the treatment. Among these techniques, FT-IR analysis is highly significant. Glass filled Rubies and Sapphires gave characteristic peaks of Si-O (glass) bonds at 2290, 2620 and 3490 cm^{-1} (Fig.5). Moreover, Synthetic corundum gemstones gave different OH stretching peaks at different locations from 3100 to 3600 cm^{-1}. Therefore, FT-IR Spectroscopy is a reliable technique to identify treated and natural Sri Lankan Rubies and Sapphires.

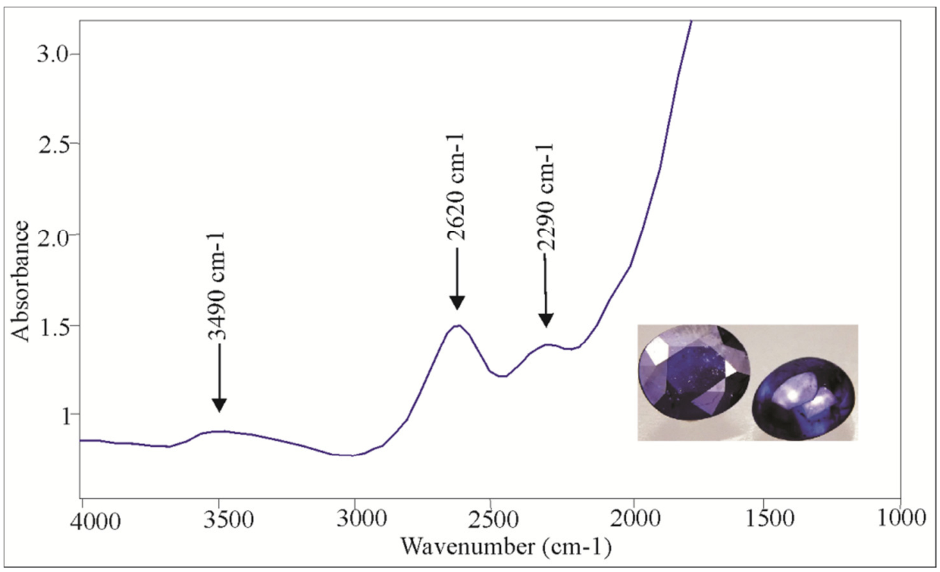

Fig.5. Glass fills (composite) sapphires giving characteristic peaks of glass (Figure modified after Leelawatanasuk et al., 2013; Christopher, 2013).

4. Remarks

There is great potential to identify treated Rubies and Sapphires in the Sri Lankan gem trade after a detailed FT-IR investigation while considering locality and geological origin.