Journal of the Korean Crystal Growth and Crystal Technology
Vol. 19, No. 2 (2009) 84-89

Nano inclusions in sapphire samples from Sri Lanka

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(Received January 12, 2009)
(Accepted January 30, 2009)

Abstract The turbid/translucent, near colorless (milky) metamorphic sapphire samples from Sri Lanka have been characterized after the heat treatment in N_2 at 1650°C. As-received sapphire specimens became bluish-colored and exhibited more clarity after the heat treatment. It was found that the color change at inclusions zoning region is attributed by the dissolution. As received samples contain the micro/nano inclusions such as rutile (TiO_2), ilmenite ($FeTiO_3$), spinel ($MgAl_2O_4$)/ulvospinel (Fe_2TiO_4) and apatite ($Ca_5(PO_4)_3$), which were dissolved by the heat treatment and form the blue color through Fe^{2+}/Ti^{4+} charge transferring. The microstructures become different because as the dissolution of apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) in alumino silicates (Al_2SiO_5) occurred, resulting in morphological change with the appearance of (Ca, Mg, Al) silicate on the surface. Both as-received and heat treated samples showed the rhombohedral crystal structure of Al_2O_3.

Key words Sapphire, Heat treatment, Nano inclusions

1. Introduction

Sapphire, a kind of mineral in corundum group (Al_2O_3), is one of the most durable gemstones. Pure sapphires typically show colorless and the various elemental impurities in sapphires make their color different. For examples, blue sapphire itself is originated from the presence of impurity elements such as iron and titanium. Nowadays, the heat treated sapphires have influenced on the gemstone market because of their great improvement on the color and clarity. Recently, sapphires from Sri Lanka have occurred in the commercial market because they can be improved to high quality-blue and yellow sapphire by the heat treatment. In particular, milky sapphires, translucent (turbid) sapphires containing needle-like rutile inclusions, can be intensified to bluish color by the heat treatment.

Wathanakul *et al.* [1] reported that the rough sapphire stones from Sri Lanka exhibit translucent appearance due to the very fine inclusions of rutile (TiO_2) and/or possible ilmenite ($FeTiO_3$) and show the developments of blue haloes around the inclusions due to the charge transfer of Fe^{2+}-O-Ti^{4+}. Other reports [2, 3] support that the silky inclusions, which is apparently seen in corundum, is presently needle-like rutile (TiO_2). There are also other inclusions such as apatite and negative crystal reported. Apatite is frequently seen in hexagonal prismatic euhedral form and can be changed into the other form more clearly than other crystalline inclusions. Moreover, liquid inclusions in rough sapphire stones look like voids in a crystal and they contain typically liquid and/or gas phase which can be often healed by heating under high temperature environment.

This work is aimed to investigate the behavior of the defects and inclusions in translucent sapphire stones from Sri Lanka after the heat treatment and demonstrate the relationship between color change and microstructural variation of sapphires.

2. Experimental

The rough sapphire stones occurring in metamorphic origin in Sri Lanka were used as starting materials. As-received stones were naturally turbid/translucent and nearly colorless. The samples were prepared by cutting into 4 specimens and polished two surfaces of each specimen using a series of diamond pastes down to 1 μm until their thickness became about 2 mm. Then specimens were cleaned in acetone and de-ionized water in an ultrasonic cleaner in order to remove all stains and impurities on the surfaces. The visual appearances of the specimens are shown in Fig. 1. The specimens were initially characterized for determining their physical and

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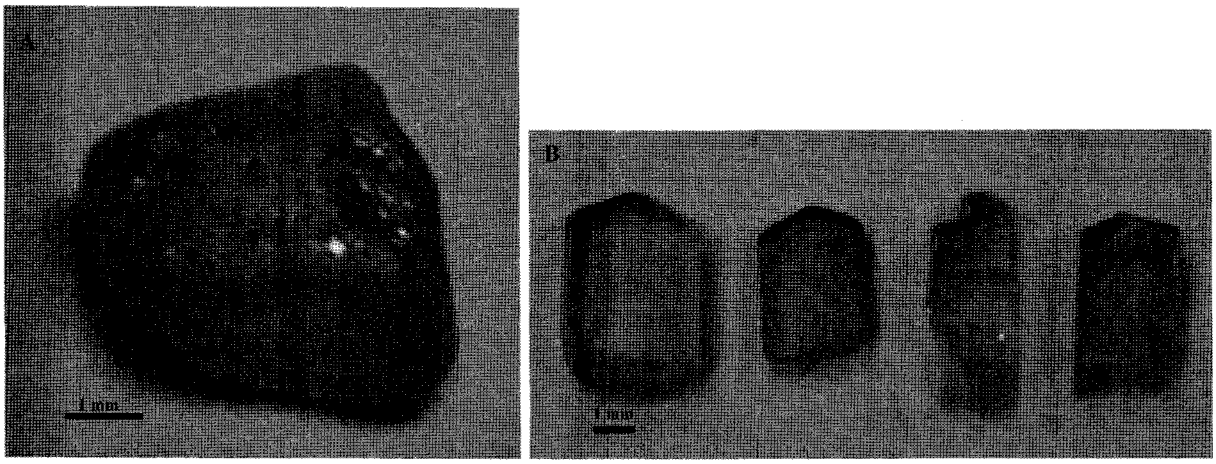

Fig. 1. The visual appearance of the samples. (A) As-received sample. (B) The 4 samples obtained by cutting.

gemological properties such as weight, color, specific gravity (SG) and refractive indices (IR). The external and internal features of specimens were observed using a transmission optical microscope (Olympus, Japan) in order to classify mineral inclusions and disclose their microstructure. Then, the major trace elements and chemical bonding characteristics of the specimens were analyzed by an UV-Vis-NIR spectrophotometer and fourier-transform-infrared-spectrophotometer (FT-IR), respectively. Scanning electron microscopy coupled with energy dispersive spectrophotometer (SEM-EDS, JEOL JSM-6700F, Japan) and transmission electron microscopy (TEM, JEOL JEM 2010, Japan) were employed for investigating the morphology, microstructure and elemental analysis on the specimen surface and revealing the crystal structure and some internal defects in the specimens. The TEM specimens were prepared by cross-sectioning by the diamond cutting machine and the polishing using a sequence of silica suspensions (0.3 μm) and diamond pastes (3 μm to 1 μm). Then TEM sample was applied for the precision ion polishing system (PIPS) for about 20 minutes depending on the sample thickness. The heat treatment was performed in an electric furnace at 1650°C for 2 hours with heating rate 5°C/min in N_2 flowing atmosphere of 500 ml/min. The same analysis for the as-received and heat-treated specimens was carried out for the comparison.

3. Results and Discussion

The polished surfaces of as-received sapphire specimens became more translucent. A few cracks were exposed on the surface and some particles were dispersed into the specimen. After heat treatment, the specimens became clearer and the blue stripes obviously appeared in the specimen as shown in Fig. 2. The FT-IR spectra of as-received and heat-treated specimens are shown in Fig. 3. As-received sample showed the peak of boehmite at 2124 cm^{-1} and H_2O bonding in the range

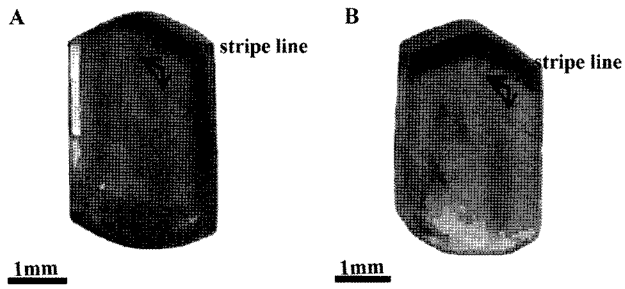

Fig. 2. The comparison of the visual appearance of sapphire samples before and after the heat treatment. (A) As-received sample (B) Blue stripes and clarity in the heat-treated sample.

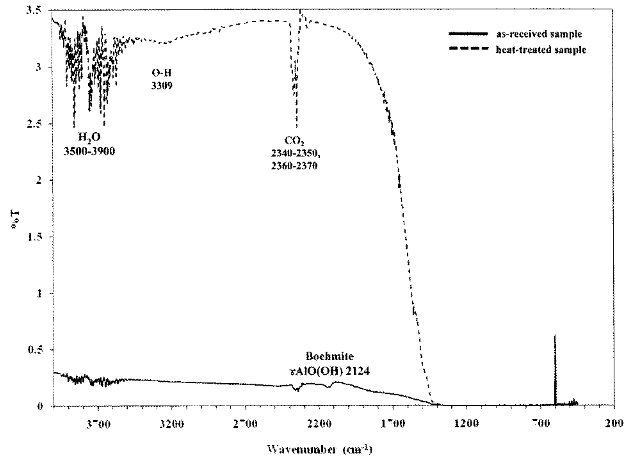

Fig. 3. FT-IR spectra of as-received and heat-treated samples.

of 3500 to 3900 cm^{-1}. Peaks in the range of 2340 to 2350 cm^{-1} and 2360 to 2370 cm^{-1} were attributed to the CO_2, resulting from the air and instrumental condition. After heat treatment, the peak of boehmite disappeared, which may be diffused into sapphire crystals, and new peak near to 3309 cm^{-1} occurred, which is related to O-H bonding [4]. The UV-Vis NIR spectra of both as-received and heat-treated specimens are given in Fig. 4. The light absorption in UV-Vis NIR analysis is directly related to the color appearance of sapphire. Both spectra showed the absorption peak of Fe^{3+} at 388 nm, corresponding to common features of milky sapphires from Sri Lanka. The heat treated specimen showed the other absorption peak of Fe^{3+} shifted to the higher wavelength of 450 nm. In addition, the charge transfer between Fe^{2+}/Ti^{4+} appeared the absorption peak at 575 nm and 588 nm, resulting in color change in Ti^{4+}-rich zoning region.

Fig. 5 shows that the as-received sapphire specimens containing needle-like rutile (TiO_2) phase and a swarm of negative crystals with fluid inclusions. Fig. 6 shows that the negative crystals appeared as distinguished shape with a specific orientation. These features have not changed even after the heat treatment. Fig. 7 shows that the brownish orange inclusions zoning is changed into bluish color especially along bands after the heat treatment, which is attributed by the dissolution of the dust and black particle. The feature of bluish band seems to be originated from the compositional variation existing in the original crystals.

There are a series of the holes with different shapes observed in the as-received specimens. After heat treatment, the holes were changed to angular shape and showed the morphology completely different from the as-received specimens. Some regions where contain the cavities became different shape and were melted. Fig. 8 shows SiO_2 phase existed in the hole and it is thought

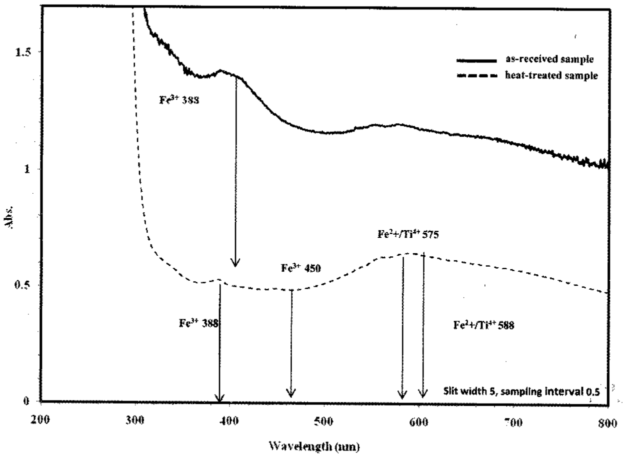

Fig. 4. UV-Vis-NIR spectra of as-received and the heat-treated samples.

Fig. 5. Needle-like structure of the rutile TiO_2 in the as-received sample.

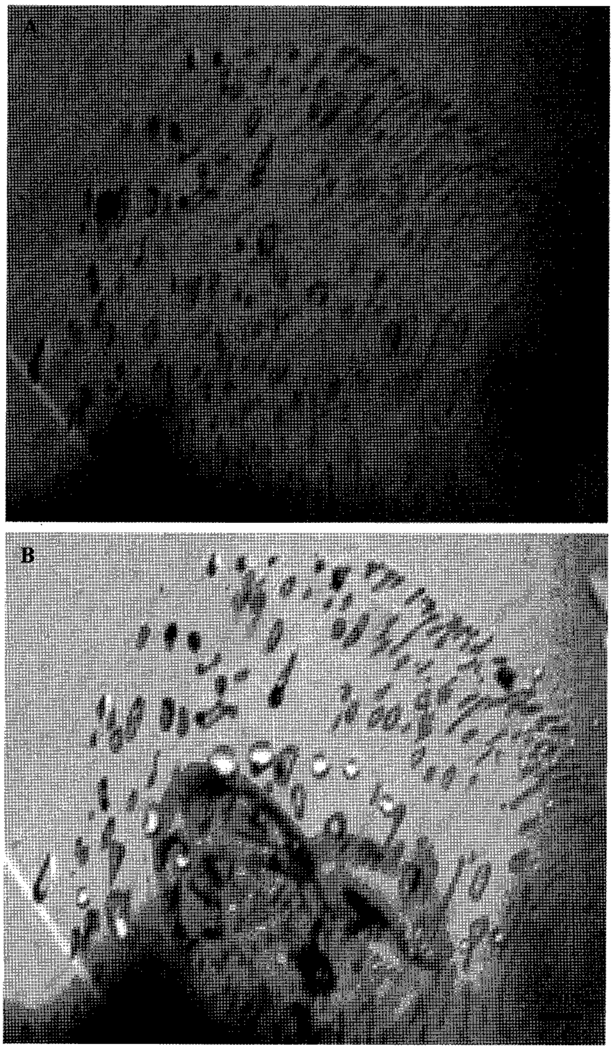

Fig. 6. Micrographs of a swarm of negative crystals. (A) As-received sample. (B) Heat-treated sample.

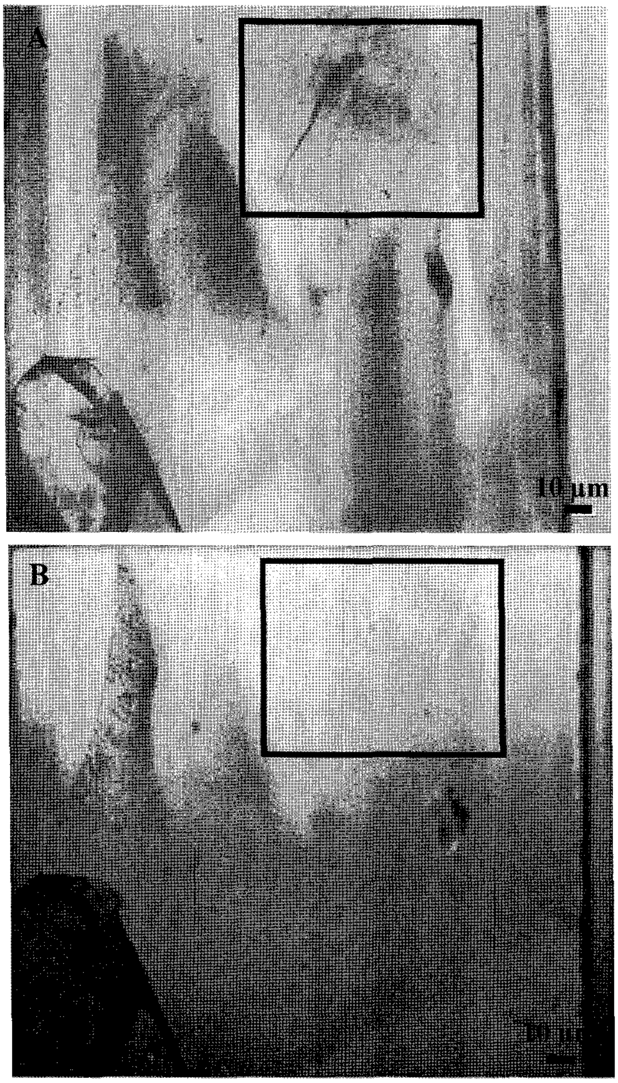

Fig. 7. Brownish-orange dust inclusions with straight lines were turned to bluish color after the heat treatment. Black particles were disappeared and the negative crystals found in sample. (A) As-received. (B) Heat-treated.

that the phase transition to monticellite ($CaMgSiO_4$) occurred after the heat treatment. Furthermore, mineral inclusions such as spinel ($MgAl_2O_4$) and pyrophyrite ($Al_2(Si_4O_{10})(OH)_2$) were dissolved into sapphire crystals and re-crystallized, resulting in the disappearance of the trigonal and feather morphology, respectively. In addition, it was found the secondary phase of apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) was transformed to (Ca, Mg, Al) silicate [5]. Fig. 9 shows another different morphology. The EDS analysis reveals the varieties of element compositions on the surface. In the case of Ti and Fe, which are the significant elements in color change of sapphire crystals, Ti was detected at the blue stripe but Fe element was not detected, which is mainly because of the smaller amounts of Fe than the detection limit.

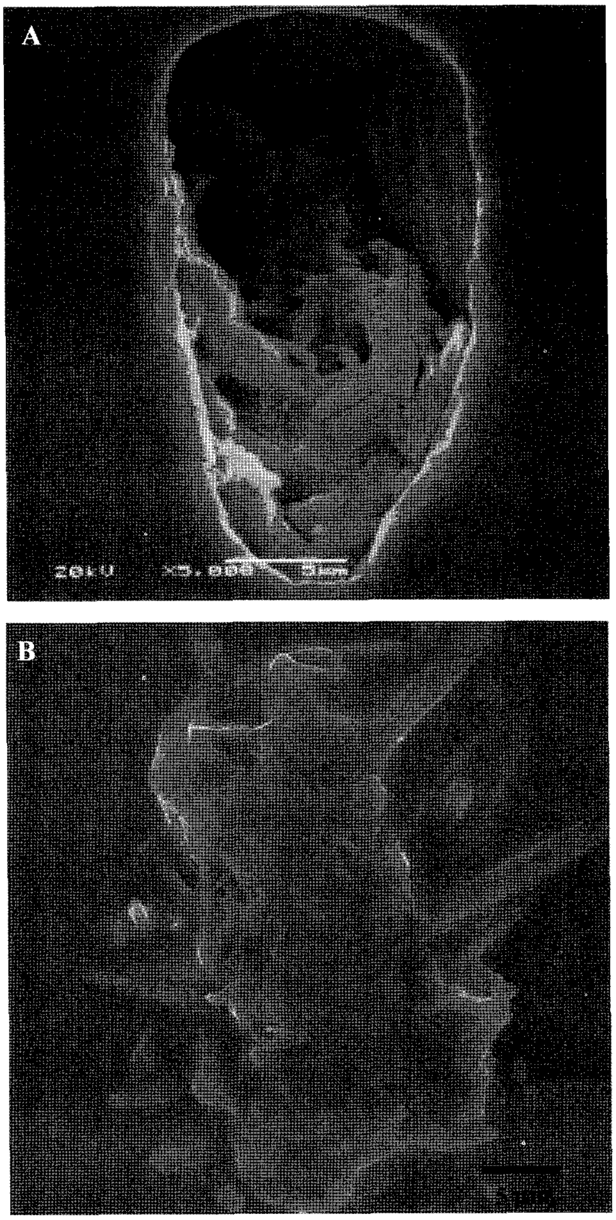

Fig. 8. Morphology change on the surface after the heat treatment. (A) As-received. (B) Heat-treated.

The TEM images and corresponding SAED patterns of the as-received and heat-treated specimens are given in Fig. 10. Both specimens show the rhombohedral crystal structure of Al_2O_3. The ring diffraction pattern in as-received specimens demonstrate the presence of micro-crystalline Al_2O_3. The dislocation structure in as-received specimen is given in Fig. 11. After the heat treatment, the striations were detected on the surface of the specimen, as shown in Fig. 12, which could be estimated to be twin defect. It is thought to be that the twin defect might be generated by the substitution of Ti^{4+} into Al^{3+} at octahedral site in sapphire structure during heat treatment where TiO_2 impurity phase broke down and Ti^{4+}

backed into sapphire structure [6, 7]. These aligned twin crystals are called by the multiple or repeated twins. If they are not in a parallel formation, they are called by the cyclic twins. Rutile phase often exhibits with the cyclic twinning shape.

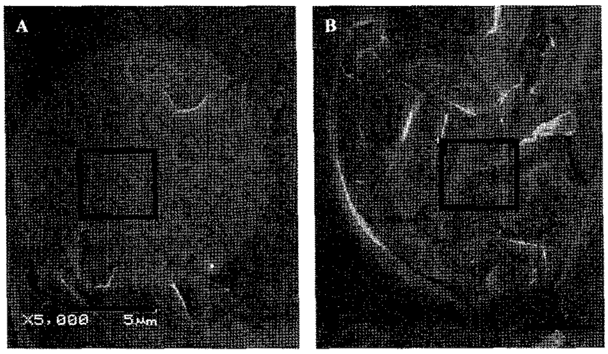

Fig. 9. Morphology change of the secondary phase after heat treatment. (A) Apatite phase in the as-received sample. (B) Ca, Mg, Al silicate phase in the heat-treated sample.

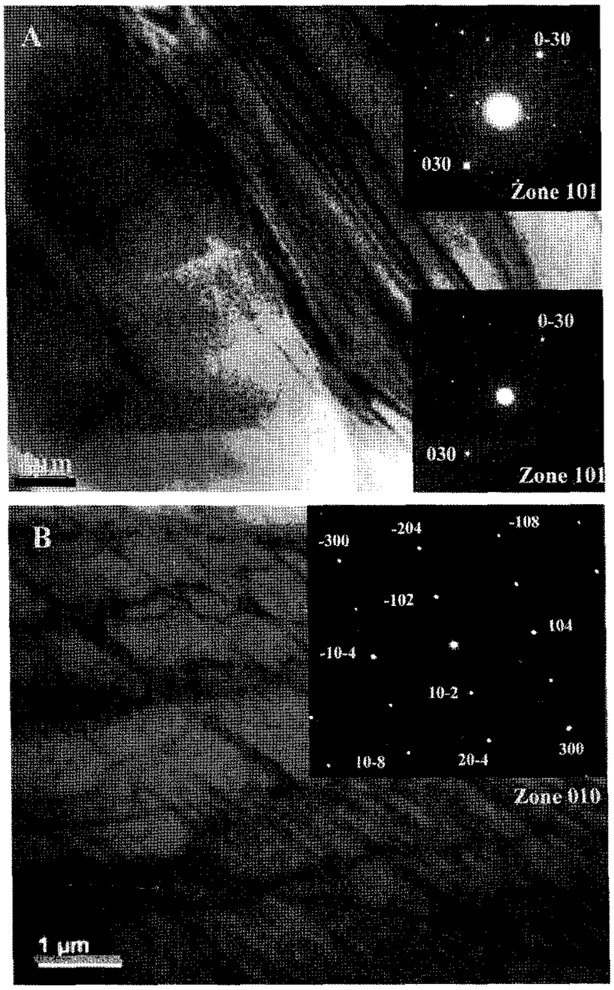

Fig. 10. TEM images with the diffraction patterns showing the rhombohedral structure of Al_2O_3. (A) As-received. (B) Heat-treated.

4. Conclusions

As-received sapphire samples from Sri Lanka contain the micro and/or nano inclusions of rutile (TiO_2), ilmenite ($FeTiO_3$), ulvospinel (Fe_2TiO_4) and apatite ($Ca_5(PO_4)_3(OH,F,Cl)$), resulting in turbid/translucent appearance. TiO_2 phase was dissolved by the heat treatment to exhibit blue color through the charge transfer between Fe^{2+}/Ti^{4+} in sapphire crystal. During heat treatment apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) phase was also dissolved and led the compositional variation of (Ca, Mg, Al) silicate. As-received sapphire samples contain the dislocation defects in rhombohedral Al_2O_3 crystal structure. It was found that the heat treatment generates the twin defects in the sapphire samples by the substitution of Ti^{4+} into the rhombohedral Al_2O_3 crystal structure. It can be concluded that the sapphire samples become more stable in

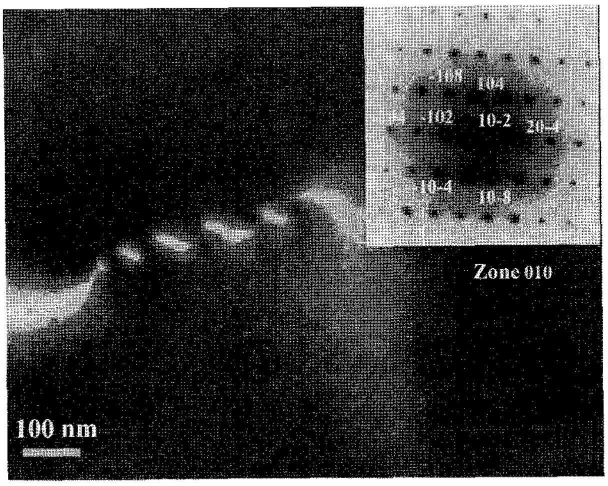

Fig. 11. TEM image with diffraction pattern showing dislocation defect in the as-received sample.

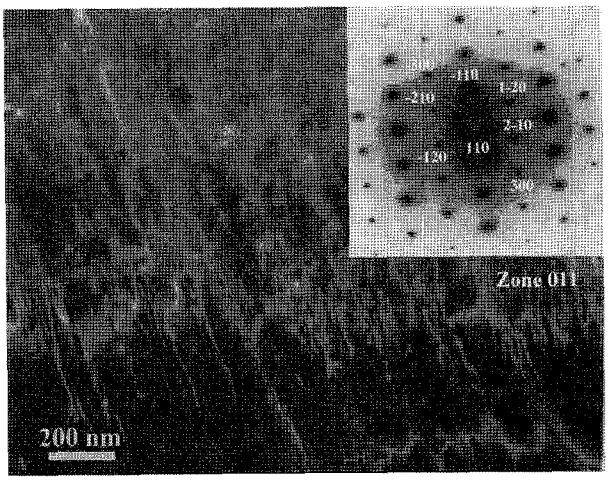

Fig. 12. TEM image with diffraction pattern showing twin defect in the heat-treated sample.

their internal structure by the heat treatment, namely the micro/nano structural rearrangement, and enhanced in terms of their color and clarity.

Acknowledgement

This study was performed with the support of the Fusion Material Program of Hanyang University (HFM), Seoul, South Korea. We would like to thank the Hanmi Gemological Institute (HGI) Laboratory for using the experimental facilities.

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