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Research Paper / Makale

The Annealing of Corundum (Ruby) in Nitrogen (N_2) Air

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Abstract: Every ruby produced in the world is in different qualities with its unique characteristics. The development of ruby's color is effective in annealing in different atmospheres. In our work, crystal parameters, spectroscopic properties and color changes were determined by heat-treating the newly discovered ruby in the nitrogen atmosphere in Turkey. The annealing result in the nitrogen atmosphere was: a-axis 0.17% and c-axis 0.25%, for R-3c: R-3c: R a-axis 7.06%, alpha angle 5.19% and a- 0.99, c-axis increased by 0.94%. After annealing, a large absorption peak was observed at a wavelength of 500 nm in the UV-Vis spectrometer. The red color of the ruby was white-light-pink after annealing. Heat treatment in the nitrogen environment caused a change in the color of the ruby.

Key words : Ruby, Annealing, Nitrogen air, Crystal parameters, UV-spectrometry.

Azot (N2) Atmosferinde Korundum(Yakut)un Tavlanması

Öz : Dünyada üretilen her yakut kendine özgü özellikleriyle farklı kalitelerdedir. Yakutun renginin geliştirilmesinde farklı atmosferlerde tavlama etkili olabilmektedir. Çalışmada, Türkiye'de yeni keşfedilen yakutun azot atmosferinde ısıl işleme tutularak, kristal parametreleri, spektroskopik özellikleri ve renk değişimleri belirlenmiştir. Azotlu atmosferde tavlama sonucu, yakutun kristal parametreleri a-ekseni % 0,88 ve c-ekseni % 0,18 oranında büyümüştür. Tavlama sonrası, UV-Vis spektrometrede 500 nm dalgaboyunda geniş absorbsiyon piki kaybolmuştur. Yakutun kırmızı rengi, tavlama sonrası beyazımsı-açık pembe renk olmuştur.

Anahtar kelimeler: Yakut, Tavlama, Azot atmosferi, Kristal parametreleri, UV-spektrofotometre

1. Introduction

Ruby is the most valuable crystal used in optical applications and as a gemstone after diamond. Ruby can behave like a laser with features such as narrow line width, long fluorescence lifetime, large quantum yield, very large absorption band, and intensifies visible light [1,2]. In the nature, ruby exists in the form of corundum (α-Al_2O_3), with the substitution of Cr^{+3} ions instead of Al^{+3} in the crystal structure. Red color formation is caused by Cr^{+3} ions. These Cr^{+3} ions are present in impurities such as Fe^{+3}, Ti^{+4}, V^{+3}, Mg^{+3} and Si^{+4}. Depending on the impurity ratio, the ruby color may vary [3,4]. On the other hand, when Al^{+3} ions are replaced by Fe^{+3}, Fe^{+2} and Ti^{+4} ions, blue corundum (sapphire) is formed [5]. Color is important in the quality of rubies. Myanmar (Burma) region is blue and purple core in the red matrix which reduces the quality of the rubies. The

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concentration of Cr, V, Ti in these blue core regions is high. In addition, blue color is the result of transfer of Fe^{+2} / Ti^{+4} intervalance change. This error can be eliminated by heat treatment at high temperature, but heat treatment increases the price. In heat treatment, ruby is kept in Bursen Burner flame. Heating time, temperature and atmosphere affect quality. At the end of the heat treatment, the ruby color disappears or the red color becomes more vivid. So it's a risky process. [6,7]. In addition, when the Myanmar rubies are annealed in an inert atmosphere at 1000-1200°C, the blue color of the ruby is slightly dispersed [3,5,8]. The stains that affect the quality of Ruby can be removed by annealing in an oxidative or reductive environment. Silky appearance can be removed with thermal curing. Heat treatments of sapphire and ruby have been studied extensively. However, many are hidden because they are commercial [5]. For this reason, a unique heat treatment is required for the development of the quality of the rubies in each country. In our study, it was aimed to determine the effective parameters in the improvement of quality by determining the crystal parameters, spectroscopic properties and color quality changes by keeping the newly discovered ruby specimens in Turkey in the nitrogen atmosphere.

2. Experimental

The ruby samples used in the study were obtained from the mines in the Doğanşehir Region of Malatya Province in 2012 in Turkey. Less quality rubies were chosen. Chemical analyzes were performed on a Rigaku ZSX X-Ray Fluorescence instrument. The measurements were carried out on glass tablets prepared by fluxing powdered samples with $Li_2B_4O_7$ in 1:10 weigh ratio. Ruby samples were cut into thin sheets. The cut samples were heated at a heating rate of 5 $^{\circ}$C / min and a peak temperature of 1200 °C for 3 hours by passing nitrogen gas through the Protherm tube furnace at a rate of 2 liters / minute. Optical properties were determined in the range of 190-1100 nm in Shimadzu UV-VIS 1200 model spectrophotometer. Phases analysis were performed with a Rigaku X-ray Diffractometer model Rint 2000 with monochoromatic filter, operating at 30 kV and 15mA (Cu-Kα, λ=1,541 A0, 2θ 5-70º, 2º/minute at a step size of 0,020). The spectra were obtained with the slits of 10 for divergence, 10 for scattering, and 0.3 mm for receiving. The phases' quantification was carried out MDI Jade 6.0 software. Phase ratios and lattice parameters were determined using the Maud 2.7 crystal structure analysis program according to the Rietveld method. 5 iterations are used in the calculations.

3. Results

The average major oxides of the samples, selected from the low-grade rubies are given in Table 1. The trace elements contained in the Ruby samples were determined as 1860 ppm Ni, 21.4 ppm Ga, 12.3 ppm Sr, 4.7 ppm Ba, 1.9 ppm Co, 5 ppm V. Compounds like corundum in nature contain trace amounts of gallium [9]. The nickel ratio is more than gallium ratio. In ruby samples, Fe_2O_3, CaO, MgO and SiO_2 were determined with Cr_2O_3. These oxides are found in the ruby structure and in the ruby formation, the detailed investigations of how these oxides inserted into the structure should be done. Fire damage is caused by diaspore $(AlOH)_3$, which is found only in low quality rubies. In dark red colored rubies, Al_2O_3 content is 99%.

Table 1. Chemical analysis of rubies

Oxides (%)											
Al_2O_3	**SiO_2**	**Fe_2O_3**	**Cr_2O_3**	**MgO**	**CaO**	**Na_2O**	**TiO_2**	**K_2O**	**P_2O_5**	**MnO**	**LOI**
95.40	0.62	0.85	0.24	0.20	0.20	0.02	0.01	<0.01	<0.01	<0.01	1.09

In the α-Al_2O_3 crystal structure, the oxygen atoms are hexagonal and the aluminum atoms are octahedral. Two adjacent aluminum atoms in the structure come over and make two AlO_6

octahedral coordination polyhedra surface-sharing. Some trivalent metal oxides may settle into the corundum structure [10]. The x-ray diffraction patterns of the ruby before and after the heat treatment in the nitrogen atmosphere are given in Fig. 1. Before the heat treatment, ruby, trigonal symmetric corundum, R-3c: H space group, R-3c: R and P-3m1 space goup corundum and 1.03% diaspore (AlOH) 3. Corundum lattice parameters, trigonal, hexagonal structure, a-axis is 4.763 Å and c-axis is 13.009 Å in the literature [11]. Lattice parameters, a-axis for R-3c: H after heat treatment 0.0083 Å, c-axis 0.032 Å; R-3c: The a-axis for R is 0.3193 Å, and the alpha angle is increased by 4.4 °. In the P-3m1 space group, the a-axis increased by 0.0461 Å and the c-axis increased by 0.1195 Å (Table 2). After the heat treatment in the nitrogen environment, the ruby lattice parameters have been increased to reach the lattice parameters given in the literature. This showed the development of crystallization and crystal regeneration. The ruby crystal structure was developed both in the a-axis and in the c-axis direction by heat treatment. Al^{+3} ions occupy two-thirds of O layers in the corundum structure. The O sites occupied are staggered because all O sites are at C positions. The occupancy of two-thirds of O sites requires that each Al^{3+} ion has an Al^{3+} ion close neighbor on one side. This causes Al^{3+} ions to be dis-placed from the normal positions of O layers halfway between layers [10]. In the Ritveld crystal refinement analysis, the trigonal crystal corundum structure was calculated according to three different space groups: R-3c:H, R-3c:R, P-3m1. In the analysis results, sig for natural ruby: 2.0982, Rwp (%): 14.291 and sig for nitrogen: 1.737, Rwp (%): 10.503. After heat treatment R-3c:H; 0.65% and R-3c:R increased by 7.28%, P-3m1; decreased by 7.93% (Table 2). The nitrogen atmosphere P-3m1 space group is effective in decreasing the ratio of the crystal to the corundum and in the regular crystal growth in the R-3c:R space group approaching 90 degrees angularly [11].

Table 2. Lattice parameters before and after heat treatment [11]

Lattice Parameters	Before Annealing			After Annealing		
	R-3c :H	R-3c :R	P-3m1	R-3c :H	R-3c :R	P-3m1
Weig. %	90.96	0.08	8.96	91.61	7.36	1.03
a-eksen, (Å)	4.7564	4.5199	4.6258	4.7647	4.8392	4.6719
b-eksen, (Å)	4.7564	4.5199	4.6258	4.7647	4.8392	4.6719
c-eksen, (Å)	12.9779	4.5199	12.6881	13.0101	4.8392	12.8076
Alpha, (º)	90	84.705	90	90	89.105	90
Beta, (º)	90	84.705	90	90	89.105	90
Gamma, (º)	120	84.705	120	120	89.105	120

The location of aluminum and oxygen atoms in the corundum structure; (0, 0, z; 0, 0, 1/2+z) for Al and (x, 0, 1/4; 0, x,1/4; x, x,1/4) for O. When the intensity ratios of Miller indices as percentages are examined before heat treatment; (012):46, (104):61, (110):36, (113):76, (024):72, (116):100 for the oxygen ions of the atoms in the crystal structure, the intensity increases only in the other planes where the intensity decreases in the plane (110) / 4) and aluminum and other impurite atoms (0,0, z), (0,0,1 / 2 + z) (Fig.1) The larger growth of the ruby c-axis after heat treatment indicates the exchange and arrangement of oxygen ions in the vacancies of aluminum and other impurite ions in the a-axis direction.

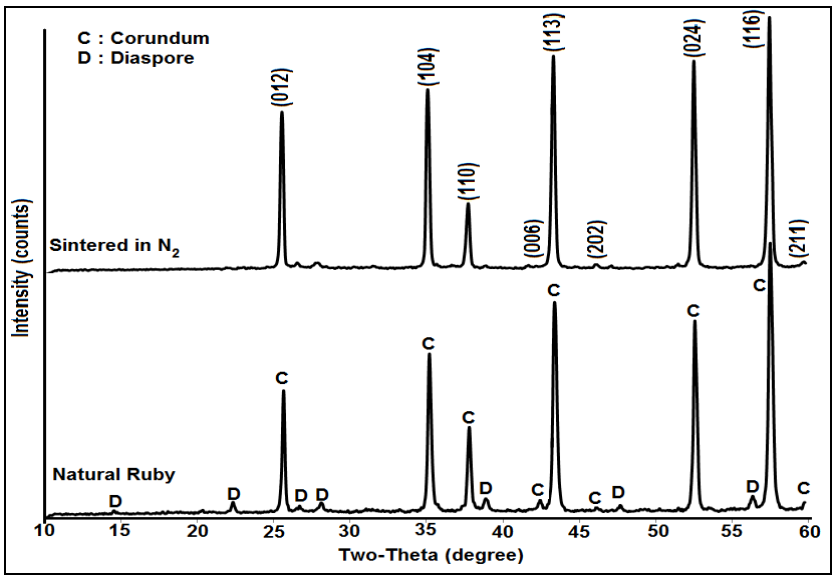

Figure. 1. Ruby X-ray diffraction patterns before and after heat treatment

The UV spectrum of the ruby before and after heat treatment in nitrogen is given in Fig. 2. Ruby, UV is very strong red in long-wave, short-wave in strong red chalky colors in blue-white [9,12,13]. The intense main absorption peak is in the form of a large hump in the range of about 200 nm and 270 nm. These peaks are caused by the oxygen vacancies that occur during F-centered crystal growth and regeneration. While the natural ruby was absent at 232 nm, there was a sharp small peak in the nitrogen environment after sintering. Natural ruby has two absorption pikes at 285 and 300nm in the UV region and a sharp absorption peak at 355nm. These absorption peaks are centered at F^{+} and F. When one or two electrons are captured by an oxygen vacancy, the F and F + centered arrangement occurs [3]. After nitrogen exposure, two peaks in the UV region resulted in absorption peaking at 300 nm as a single peak, and disappearance at 355 nm peak, leading to F-centered regulation of oxygen vacancies in the nitrogen atmosphere. More oxygen vacancies occur when Cr^{+3} enters the α-Al_2O_3 lattice [3,14]. The formation of oxygen vacancies is caused by reductive conditions [1,15]. Typical absorption peaks of Cr^{+3} in Ruby were observed as broad absorption peaks between about 365-485 nm and 490-630 nm. These absorption peaks are associated with the chromium (Cr^{+3}) +3 valance state, with two absorption peaks corresponding to $^4A_2 \rightarrow {}^4F_1$ (U band) and $^4A_2 \rightarrow {}^4F_2$ (Y band) energy transitions [3,1,16]. These peaks are effective in the iron, nickel, magnesium and calcium elements that are present beside the chrome of the ruby in the broad absorbing pike. The effect of Cr^{+3} and Fe^{+3} and Ni^{+3} ions on these two broad peaks in ruby is 455nm and 570nm respectively. In the sintered ruby, the absorption peaks of 570 nm disappear and very broad peaks occur in the wavelength range of 360-640 nm. The luminescence behavior of Cr-doped alumina under 410 nm light excitation depends on the phase composition or crystal structure of the host alumina. Cr-doped α-Al_2O_3 powders (its single crystal ruby) typically show R-line fluorescence at the octahedral region at 694 nm ($^2E_g \rightarrow {}^4A_{2g}$) for Cr [16,17]. In the broad characteristics, the absorption peak at 690-705 nm (near 700 nm or 1.8 eV) corresponds to the R-line peak [14,18]. This R-line absorption peak $^4A_2 \rightarrow {}^2E$ optical transition outcome. R_1 and R_2 are sharp and weak absorption peaks close to 694 nm. The absorption peak at 690-705 nm (near 700 or 1.8 eV), corresponding to the R-line peak, is evident at 697 nm with narrow characteristics, but this peak is not very evident after sintering. In the Cr-doped α-Al_2O_3 structure, the transition from $^2E_g \rightarrow {}^4A_{2g}$ changed the R-line peak by changing the octahedral region. The α-alumina phase gives narrow bands in the 670-720 nm region while the δ-alumina phase gives a large emission band at the crystal lattice 750 nm. The most common impurities affecting the luminescence properties of Al_2O_3 are Fe, Ti, Cr transition metals and provide long wavelength emission. In the different forms of alumina, a broad-band emission band is observed at 700-900 nm [12,13]. After heat treatment,

ruby gave a broad absorption peak at very low height after 800nm wavelength. This very wide hunch is not seen before the heat treatment.

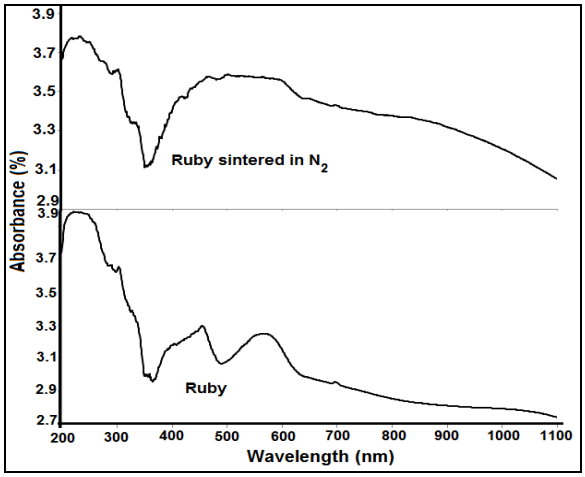

Figure. 2. UV-VIS spectrometers of raw ruby and annealed in N_2

The presence of chromophore elements in the natural ruby structure, the ratio and the geological formation environment are influential in color quality. The natural ruby redness (Fig. 3A) is darker than the heat treated ruby. In the nitrogen environment, the color of the ruby is pinkish by heat treatment (Fig. 3B). Also the surface is whitish. This whitish appearance is seen as very thin vein like lines on the surface. After the heat treatment of the ruby, the color is whitish, light pink. While the red color of Ruby occurs with Cr^{+3}, the blue color of sapphire usually changes according to the charge transfer of Ti^{4+} -Fe^{2+} and Fe^{2+} -Fe^{3+} pairs. Yellow color occurs with Fe^{3+} or Mg-centered holes [19-21]. Ruby may contain Ti, V, Ga in trace amounts together with Cr, Fe. Sapphire synthesizes chromium red, nickel yellow, chromium + nickel pinkish orange while producing titanium and iron blue surface [7,22,23]. Changes in the valance values of the elements Fe, Mg, Ca, Ni in the case of the pink color of the ruby color after heat treatment in the nitrogen atmosphere, the heat regulation of these elements in the crystal structure and the changes in the oxygen vacancies are influential.

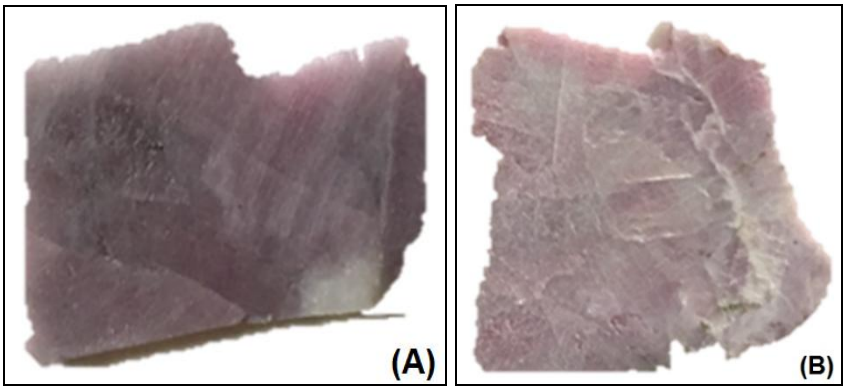

Figure. 3. In nitrogen atmosphere, before and after heat treatment (A) and after (B) ruby appearance

4. Conclusions

In the nitrogen atmosphere, crystal lattice parameters of the heat treated oxygen ions (0,x,1/4) and aluminum and other impurity ions (0,0,z), (0,0,1/2+z) Heat treatment in nitrogen atmosphere resulted in an R-3c:H a-axis 0.17%, c-axis 0.25%, R-3c:R-axis 7.06%, alpha angle 5.19% and P-

3m1 an increase of 0.94%. The highest change in the nitrogenous environment was in the R-3c: R space group, and then the P-3m1 group in the crystal structure. It is evident that the crystal structure of the ruby has evolved both in the a-axis and in the c-axis direction as a result of the heat treatment in the nitrogen atmosphere. Due to this structural change, the natural ruby UV-VIS spectrometers combine broad absorption peaks between approximately 365-485 nm and 490-630 nm, resulting in a single broad absorption peak at annular wavelengths of 360-640 nm. In addition to the chromium present in the ruby, the large absorption in Fe, Ni, Ca and Mg elements is also effective in the formation of pigments. The presence of these elements in the ruby structure and the three hours of heat treatment in the nitrogen environment caused a reduction in the red color of the ruby, resulting in a lighter red-pinkish color. The surface of the ruby that is annealed is whitish in the form of capillaries. The color change, together with the inclusions, is the structural adjustment of the oxygen vacancies by heat treatment. In addition, oxygen vacancies in chromium, iron, nickel, calcium, magnesium atoms are affected by both the a-axis and the c-axis heat effect. In these structural arrangements, the lattice structure expands by increasing the lattice parameters in the a-axis and c-axis directions. In the nitrogenous environment, the heat treatment of the ruby for three hours is effective on the lattice parameters, which causes the change in the ruby color. It has been determined that the color quality is not developed by heat treatment of the ruby in the nitrogen atmosphere for three hours, but the color is pink and the ruby color quality is ruined by the disappearance of the redness. The main reason for this is the presence of iron, magnesium, nickel and calcium atoms associated with chromium in the oxygen vacancies during heat treatment. The presence of impurite atoms found in ruby structure, heat treatment atmosphere, temperature and duration will be investigated in detail and the optimum parameter values will be improved by heat treatment in ruby color and quality [11].

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