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LA-ICP-MS Study of Impurity Ion Concentrations in Zircon

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ABSTRACT

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is surface-sensitive analytical technique for the estimation of element concentrations as well as their spatial distribution in the analyzed sample. In this work, LA-ICP-MS technique was used for analyzing the impurity ion concentrations in zircon. Because the presence of the impurity ions in the zircon usually caused the color in crystal, the zircon samples in this study are divided into three major groups i.e. untreated zircon (brown color), heat treated zircon in oxygen atmosphere (yellow color) and heat treated zircon in argon atmosphere (greenish blue color). For the first group, the most impurity ion concentrations are Fe (208.90 ppm) and Ti (91.24 ppm). For the second and third groups, there are Fe (965.88 ppm) and Mg (412.20 ppm), Fe (434.66 ppm) and Ti (109.26 ppm), respectively.

Key words: LA-ICP-MS, impurity ions, zircon

INTRODUCTION

Zircon has been known as one of the most popular precious gemstone because of the remarkable range observed in its specific gravity and its refractivity (Smith, 1972). It has a wide variety of impurity ions, rare-earth ions and several transition ions. The most of zircon generally occur as dull and dark crystals which are not colorful and bright for jewelry trading.

Heat treatment is the important method to color enhancement of gemstones. Each type of gemstone has different conditions of heat treatment. Moreover the process can vary the factor such as temperature, atmosphere and heating time. The effects of color changes under oxidation or reduction heat treatment due to any transition metal ions present (Winotai *et al.*, 2001).

In recent year, the surface-sensitive techniques were used to analyze the gemstones, e.g. secondary ion mass spectrometry (SIMS) (Steven *et al.*, 2004), X-ray photoelectron spectroscopy (XPS) (Achiwawanich *et al.*, 2006), electron microprobe analysis (EMPA) (Arnaud *et al.*, 1997), particle induced X-ray emission spectrometry (PIXE) (Sanchez *et al.*, 1997), ultra –violet laser ablation microprobe (Wartho *et al.*, 1999) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Guillong *et al.*, 2001). LA-ICP-MS has been established in many analytical laboratories because it is an efficient surface and bulk analytical technique for the estimation of element concentrations as well as their spatial distribution

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in the analyzed sample. LA-ICP-MS is highly sensitive when compared to SIMS and it is easy to prepare the sample (Zoriy *et al*., 2006). Due to its major advantage in high sensitivity, LA-ICP-MS has been used in this work for analyzing the impurity ion in zircon. This experimentation concludes that the LA-ICP-MS technique is capable of analyzing the impurity ion concentration in various gemstones. The results prove that this technique is faster and more accurate that other techniques, e.g. XRF. This is because the technique of interest is highly sensitive with the detection limit less than 100 ppm. Therefore, the LA-ICP-MS technique can measure and analyze the trace elements in smallest quantity with ease.

MATERIALS AND METHODS

Laser ablation analyzer was performed using a CETAC laser ablation system (model LSX-500) with Q switched Nd:YAG, operating at 266 nm. The experimental parameters used for the analysis of zircon are summarized in Table 1. The zircon samples are divided into three groups i.e. untreated zircon, heat treated zircon in oxygen atmosphere and heat treated zircon in argon atmosphere. The diameters of all samples approximately are 5 mm and the spot size of laser crater was 150 μm. Two lines were scanned through the analyzed cross-section. The LA-ICP-MS was calibrated to element concentrations (ppm) using NIST Standard Reference Material (SRM). For calculating impurity ion concentrations, we have assumed that all impurities are located in micro-inclusion. The impurity ion concentrations are calculated after the following equation

$$CAS = \frac{I_{AS} * C_{AR} * C_{ZrS} * I_{ZrR}}{C_{ZrS} * I_{AR} I_{ZrR}}$$

where C_{AS}, C_{AR}, C_{ZrS} and C_{ZrR} are the concentration of analyzed sample, reference standard, zirconium in sample and zirconium in the reference standard, respectively. I_{AS}, I_{AR}, I_{ZrS} and I_{ZrR} and are the intensity of analyzed sample, reference standard, zirconium in sample and zirconium in the reference standard, respectively.

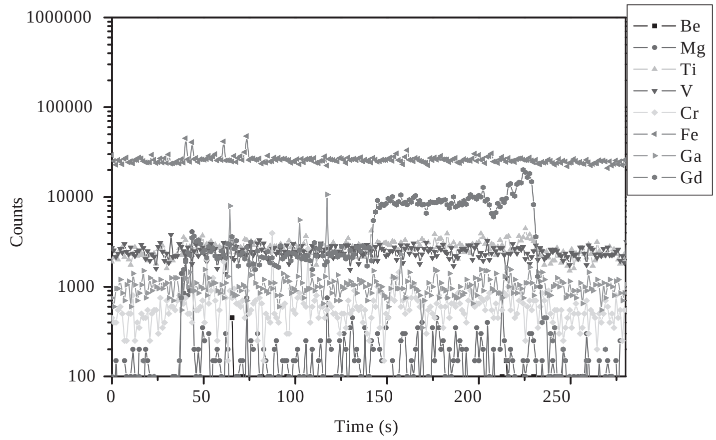
For calculation, we assume that one particular zircon crystal have 85% Zr ion concentrations. By assumption, the rest of zircon crystal should have the same amount of Zr ion concentrations with respect to the first crystal.

RESULTS

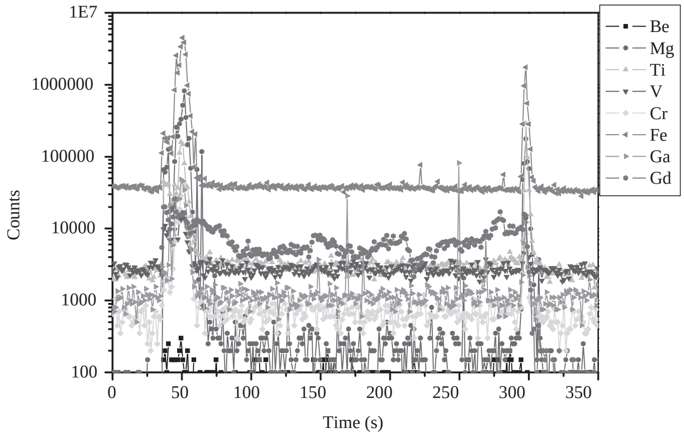
The transition elements (Be, Mg, Ti, V, Cr, Fe, Ga and Gd) in untreated zircon (brown color), heat treated zircon in oxygen atmosphere (yellow color) and heat treated zircon in argon atmosphere (greenish blue color) were investigated using LA-ICP-MS. The time-resolve plots of the raw data are shown in Figure 1. All impurity ions are homogeneously distributed in the untreated

Table 1 LA-ICP-MS instrumental parameters used for elemental analysis.

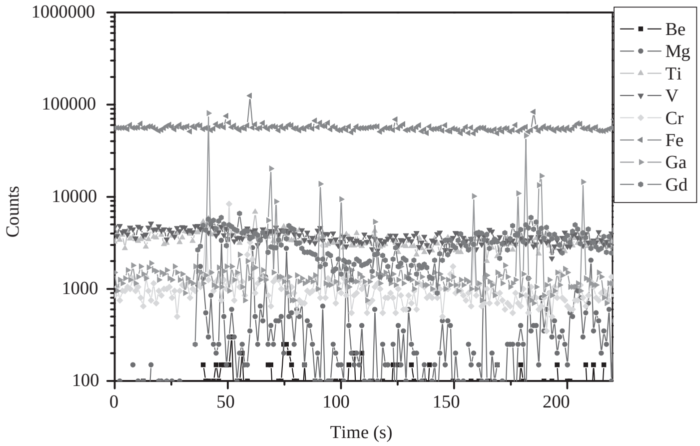
Parameters	Value
Wavelength of Nd:YAG laser (nm)	266
Laser scan speed (μm sec^{-1})	40
Plasma gas (l min^{-1})	14
Argon as carrier gas after cell (l min^{-1})	0.4
Helium as carrier gas through cell (l min^{-1})	1
Ablation mode	single spot
Spot size (μm)	150
Energy output (%)	100
Frequency (Hz)	20



(a)



(b)



(c)

Figure 1 Time-resolve data plot of (a) untreated zircon, (b) heat-treated zircon in oxygen atmosphere and (c) heat-treated zircon in argon atmosphere showing the selected elements (^{9}Be, ^{25}Mg, ^{49}Ti, ^{51}V, ^{52}Cr, ^{53}Fe, ^{69}Ga, ^{158}Gd). Each point is ablated for 40 s.

Table 2 The impurity ion concentrations (in wt-ppm) of the three zircon samples.

Sample	Be	Mg	Ti	V	Cr	Fe	Ga	Gd
Untreated zircon	4.28	17.21	91.24	5.83	16.12	208.90	5.48	74.61
Heat-treated zircon in oxygen atmosphere	8.42	412.20	316.56	7.55	37.75	965.88	10.74	99.78
Heat-treated zircon in argon atmosphere	12.76	16.42	109.26	8.03	24.87	434.66	9.64	53.00

zircon and heat-treated zircon in argon atmosphere. On the contrary, impurity ion concentrations of interest are all found at both edges of the heat-treated zircon in oxygen atmosphere rather than the near-center of the zircon, as shown in Figure 1(b). The averages of impurity ions concentrations in each sample are shown in Table 2. From the experiments, Iron has been found as the highest concentrations in the three groups of zircon, especially in heat-treated zircon. in oxygen and argon atmosphere and untreated zircon, respectively. Other discovered impurity ions, in descending order of ion concentrations, are Mg, Ti, Gd, Cr, Be, Ga, and V respectively. Ga and V have been found in little quantity, they are not significantly important to consider.

DISCUSSIONS

From the results, all zircon samples exhibit the highest concentration of Fe. In general, the samples with Fe impurity will change its color in yellow to reddish brown, depending on the impurity ion concentrations, types and structures of the samples. The experimental results also correspond to the above, that is, the samples of interest show only colors of yellow and brown. Nevertheless, the tendency of the impurity ion concentrations does not directly proportional to the darkness of the color. In these experiments, for example, the samples of higher impurity ions concentrations are yellow, while the samples of lesser impurity ion concentrations are reddish-brown. Ever though these samples come from the same occurrence, they all have different initial conditions of the gemstones themselves, both prior to and after heat treatment. Therefore, the relationship of the impurity ion concentrations and the darkness of the color cannot be directly compared in the experiments.

CONCLUSION

The untreated zircon has Fe(208.90 ppm) and Ti(91.24 ppm) as the highest impurity ion concentrations. The heat-treated zircon in oxygen atmosphere has Fe(965.88 ppm) and Mg(412.20 ppm), while the heat-treated zircon in argon atmosphere has Fe(434.66 ppm) and Ti(109.26 ppm) as the highest impurity ion concentrations, respectively. In addition, heat treatment and atmosphere have effect to the distribution of the impurity ions.

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