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Trace Elements and Colors in Gemological Varieties of Spodumene Mineral

M.A.S.Lacerda, E.F.Oliveira, R.Stasiulevicius, G.F.Kastner, A.M.Amaral
Centro de Desenvolvimento da Tecnologia Nuclear, Comissão Nacional de Energia Nuclear, Belo Horizonte, Brazil.

ABSTRACT: This work presents the results of characterization and irradiation treatment of two spodumene mineral varieties (greenish and lilac). To determine the concentration of trace elements in the samples the k_0 Instrumental Neutron Activation Analysis (*k_0-INAA*) was used. A ^{60}Co irradiator was used for the treatment of the specimens. The change of color, when they were submitted to high intensity gamma rays, was analyzed. The results obtained in characterization and irradiation treatment showed relatively good agreement with the literature. The *k_0-INAA* method, showed its potential as an analytical multi-elemental determination tool. Some elements in trace quantities were detected in the samples, suggesting a possible influence of these elements on spodumene colors.

1 INTRODUCTION

The spodumene mineral, from pyroxene group, represented by the general formula $LiAlSi_2O_6$, is a source for the production of Li salts. The transparent varieties of beautiful coloration are gemstones.

Gemological varieties of spodumene are rare in nature, being known as kunzite (lilac) and hiddenite (green). Colorless, yellow-straw and pale-green varieties do not have specific denominations.

Mineral varieties show well-known coloration changes whenever they are submitted to gamma rays, X-rays, electrons, and ultraviolet rays. Most authors associate the coloration change, as well as the luminescence phenomenon presented by some spodumene varieties, to the main impurities concentration: Mn, Fe and Cr (Claffy 1953; Holuj 1968; Webster 1970; Ito 1980; Fujii & Isotani 1988; Isotani et. al. 1991).

This work presents the results of characterization and irradiation treatment of some spodumene mineral varieties. The k_0 Instrumental Neutron Activation Analysis (*k_0-INAA*) was used to determine the concentration of trace elements in 4 samples of 2 varieties (greenish and lilac) of spodumene mineral. The *k_0-INAA* is a non-destructive technique that provides an accurate multielemental analysis (De Corte 1986; Menezes et al. 2003). It has long been one of the most sensitive used to measure the concentration of trace amounts of many elements in gemstones.

2 EXPERIMENTAL

Lilac and greenish varieties of spodumene obtained in Minas Gerais, Brazil, were analyzed. The samples, weighing about 300 mg, were irradiated in the reactor Triga Mark I IPR-R1 (100 kW – neutron flux of $6.6 \cdot 10^{11}$ n . cm^{-2} . s^{-1}) in the Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN), Belo Horizonte, Brazil. Reference certified material of International Atomic Energy Agency (IAEA/Soil-7) was simultaneously irradiated for quality control purposes.

The *k_0-INAA* in lower layer rotatory rack was applied using Na as comparator. Trace elements concentrations were determined through three schemes of irradiation performed in rotary rack: (i) 4 minutes of irradiation time, 2-15 minutes of decay time and about 10 minutes of measuring time to determine short half-life isotopes; (ii) 4 hours of irradiation time, 36-48 hours of decay time and about 3 hours of measuring time to determine isotopes with medium half-life values and; (iii) 16 hours of irradiation time, 20-25 days of decay time and about 6 hours of measuring time to determine long half-life isotopes.

Gamma-spectroscopy analysis was performed in two coaxial CANBERRA HPGe detectors, models GC1518 and GC5019, coupled to a multichannel analyzer. The first detector was used to determine long half-life isotopes and the second one to determine short and medium half-life isotopes. Technical problems did not allow the use of the same detector model for all measurements.

Color changes on spodumene samples, when they were submitted to high intensity gamma rays, were analyzed too. A ^{60}Co irradiator, with activity of about 40.000 Ci was used for this approach.

3 RESULTS AND DISCUSSION

Major and trace elements concentrations of reference certified material and samples are listed in Tables 1 and 2, respectively.

Table 1. Experimental and certified elemental concentrations (in µg . g^{-1}) for IAEA/SOIL-7 reference.

Element	E.V	C.V	C.I
Al	49442 ± 9400	47000	44000 – 51000
As	15.8 ± 0.6	13.4	12.5 – 14.2
Ce	49.6 ± 0.5	61	50 – 63
Co	8.5 ± 0.2	8.9	8.4 – 10.1
Cr	42.3 ± 0.5	60	49 – 74
Cs	5.0 ± 0.2	5.4	4.9 – 6.4
Cu	ND	11	9 – 13
Dy	4.9 ± 0.4	3.9	3.2 – 5.3
Fe	24455 ± 82	25700	25200 – 26300
Ga	8.7 ± 1.4	10	9 – 13
K	11533 ± 127	12100	11300 – 12700
La	25.2 ± 0.2	28	27 - 29
Mn	679 ± 2	631	604 – 650
Na	2402 ± 34	2400	2300 – 2500
Rb	ND	51	47 – 56
Sb	ND	1.7	1.4 – 1.8
Sc	7.3 ± 0.2	8.3	6.9 – 9.0
Ti	ND	3000	2600 – 3700
V	59.5 ± 15	66	59 – 73

E.V: Experimental values; ND: Not detected
C.V: Certified values; C.I.: Confidence Interval

Table 1 shows that experimental results present good agreement with certified values. Some elements were not determined due to inherent interference. These results also agree with previous analyses performed in Radiochemical Laboratory in CDTN (Menezes et. al. 2003) and permit to check the reproducibility and accuracy of experimental results for spodumene mineral samples.

Table 2. Major and trace elements concentrations (in µg . g^{-1}) in 4 samples of 2 varieties (greenish and lilac) of spodumene mineral.

	Greenish varieties		Lilac Varieties	
Element	A	B	A	B
Au	< 0.5	< 0.5	< 0.5	< 0.5
Ce	16.0 ± 3	18.0 ± 3	15.9 ± 2	10.2 ± 1
Cr	ND	ND	ND	ND
Fe	440 ± 50	925 ± 30	280 ± 30	195 ± 30
Ga	42.8 ± 3	43.0 ± 2	145 ± 4	53 ± 3
Hf	ND	ND	< 0.5	< 0.5
K	670 ± 70	620 ± 50	530 ± 100	420 ± 90
La	8.6 ± 0.5	7.5 ± 0.5	5.5 ± 0.5	4.7 ± 0.5
Mn	470 ± 10	490 ± 10	840 ± 10	390 ± 10
Na	990 ± 50	830 ± 50	1170 ± 50	1180 ± 50
Os	3.1 ± 1.1	3.0 ± 0.5	ND	ND
Rb	ND	ND	3.6 ± 0.7	ND
Sc	15.5 ± 0.5	17.1 ± 0.5	< 0.5	< 0.5
Sm	< 0.5	< 0.5	< 0.5	< 0.5
V	14.5 ± 2	17.6 ± 2	ND	ND
[Fe]/[Mn]	0.93	1.89	0.33	0.50

Table 2 shows an approximate Mn content in two samples of greenish spodumene. The sample B shows much higher Fe concentration. Probably, the high concentration of Fe is associated to the green color of the samples, once the greenish varieties of spodumene sampled are not true hiddenite: they are not coloured by chromium (Webster 1970). On the other hand, as the [Fe]/[Mn] ratio is low (< 2) the samples are not intense green. Contrary to green varieties sampled by Fujii & Isotani (1988).

The Mn appears in higher concentration in lilac samples. This fact is probably associated to the lilac color of these spodumene samples.

Considerably high concentration of Ga and low concentration of La and Ce in all the samples were }detected. Os was detected only in greenish samples and Sc present a much higher concentration in greenish compared to the lilac samples. These elements may be substituting Al in $LiAlSi_2O_6$ crystal.

V was detected only in greenish samples and Cr was not detected in the studied samples (probably, its concentration is below the detection limit). Vanadium in the samples is too low in concentration to cause the green color.

High concentration of Na and K was found in all the studied samples. These elements may be substituting Li in $LiAlSi_2O_6$ crystal.

Irradiation of the greenish samples to high intensity gamma-rays from ^{60}Co irradiator (radiation dose of about 20 kGy) did not influence the color of these samples. But, lilac spodumene turned deeply green under gamma irradiation. When heated to temperatures above 120 ºC the green color disappears in a few hours. This fact, already observed in the literature (Claffy 1953; Holuj 1968; Webster 1970; Ito 1980; Fujii & Isotani 1988;

Isotani et. al. 1991), may be associated to higher Mn concentration and the great mobility of Li ion in the crystal force field.

4 CONCLUSION

The results obtained in characterization and irradiation treatment of two varieties of spodumene mineral (greenish and lilac) showed relatively good agreement with the literature.

The k_0-*INAA* method, applied for trace elements determination in samples, showed its potential as an analytical multi-elemental determination tool. Applying this technique was possible to identify some elements in trace quantities. Some of these elements, as V, Fe and Mn, found in samples, may suggest a possible influence on color which the spodumene possess. Since the color of spodumene is a complex function of Mn/Fe/Cr/V concentrations and valence states, to determine only trace elements concentrations is not sufficient to solve the problem.

5 ACKNOWLEDGMENT

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