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Pixe Analysis of Precious and Semi Precious Gem Stone Minerals of Alexandrite (Beo.al2o3) of Chrysoberyl Gem Stone and Chrysoberyl Cats Eye, Visakhapatnam From Parts of South India

Chemistry

KEYWORDS : PIXE, Alexandrite, Chrysoberyl, Chrysoberyl Cat's Eye, Ruby, Corundum, Moonstone, Garnet, Tourmaline, Sillimanite Cat's Eye

D.V.L.SIRISHA Dept. of P.N.C.O, A.U; Visakhapatnam, India

ABSTRACT *PIXE method is a non-destructive technique of elemental analysis, comprising a detector, the amplifier, spectroscopy amplifier, analog to digital convertor, multi-channel analysis and an output device. Sample is presented to a detector and the results are stored in the digital form. In the present study, five elements namely Fe, Al, Mn, Cr and Se were determined in addition to the rare earth elements. The distinction of chrysoberyl / chrysoberyl cat's eye and alexandrite is also determined due to the variation of the concentration by the element chromium. Chromium recorded higher concentration up to 4.92% from 0.92% due to the intensity of colour change of mineral from green to red under incandescent light. This forms a major contribution of the present investigation.*

INTRODUCTION: In research, the classification is made by studying the presence of major elements such as Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K,P and others. Samples of Chrysoberyl and Chrysoberyl cat's eye gemstones, obtained from Visakhapatnam District, Andhra Pradesh, were analyzed for their multielement profiles by both relative and ko instrumental neutron activation analysis (INAA). Samples were irradiated in Apsara reactor and radioactive assay was carried out using high-resolution gamma ray spectronmetry. Results of about 13 elements are presented in this paper. The accuracy of the method was evaluated using IAEA CRM soil-7.

Seven Chrysoberyl samples; PSP-CBI, PSP-CB2, PSP-CB3, PSP-CB4, PSP-CB5, PSP-CB6, PSP-CB7 were collected from different parts of Pappusettipalem Village, Golugonda Mandal, Visakhapatnam District, Andhra Pradesh, India whereas the six Chrysoberyl cat's eye samples; PSP-CBCE1, PSP-CBCE2, PSP-CBCE3, PSP-CBCE4, PSP-CBCE5, PSP-CBCE6 were collected from different parts of Pappusettipalem village of the same district. Multi-element analysis using both relative and k0 instrumental neutron activation analysis has been carried out and results are discussed in this paper.

Materials and Methods:

***Sample collection and Preparation*:**

Gemstone samples were powdered separately using an agate mortar and were sieved with 320um mesh. Accurately weighed samples of 50-100 mg were packed in alkathene and were doubly sealed. Samples, IAEA Certified reference material Soil-7 (CRM Soil-7) and a gold standard were irradiated using both Apsara and pneumatic carrier facility (PCF) of Dhruva reactor. The samples were assayed using high-resolution gamma ray spectrometer consisting of a 40% HPGe detector.

Equipment:

The 3MeV Proton beam obtained from tandem type pelletron accelerator at IOP (Institute of Physics), Bhubaneswar, India.

Results and Discussion:

The measured elemental concentrations for Chrysoberyl and Chrysoberyl cat's eye samples are given Tables 1 and 2, respectively. The uncertainties on the measured concentrations (Tables 1 and 2) are the unweighed standard deviations from four independent measurements at $\pm$ 1s confidence limit. A total of 13 elements were measured in Chrysoberyl cat's eye samples (Table 1) and 12 elements in Chrysoberyl are measured (Table 2) of the seven key elements in the gem stones viz., Mg, Fe, Al, Mn, Cr, V and Sc only Cr, Mn, Sc and Fe were measured from long irradiations whereas others were measured by short irradiations. Chrysoberyl cat's eye and Alexandrite are two varieties of Chrysoberyl. The colours of various types of gemstones are due to the optical absorption spectrum in the range of 380 to 760 nm of visible region facilitated by the presence of chromophoric transition metal ions. To evaluate the accuracy of the method IAEA certified reference material CRM SL-3 (Lake Sediment) was analyzed.

Gemstone samples were powdered separately using an agate mortar and were sieved. Accurately weighed samples of 50-100 mg were packed in polythene and were doubly sealed. Samples, IAEA Certified reference material, CRM SL-3 and a gold standard were irradiated using both Apsara and pneumatic carrier facility (PCF) of Dhruva reactor. The samples were assayed using high – resolution gamma ray spectrometer consisting of a 40% HPGe detector, in an efficiency calibrated detector to sample geometry. Characteristic peak areas, determined by PHAST software, were used to arrive at the elemental concentrations.

The elemental concentrations of 16 elements determined in alexandrite samples are given in Table 1 the results obtained for the CRM SL-3 are given in Table 2. The concentration values of A1, Dy and Mn were determined from short irradiations using PCF and the concentration values for other elements were obtained from long irradiations. The elemental concentrations given in the above-mentioned tables are in mg/g (ppm) unless mg/g is specified. The uncertainties quoted on the measured elemental concentrations in these tables are at 1q precision level and these uncertainties are unweighed standard deviation computed from four independent measurements. The uncertainty varied from less than 1% to 10% depending on the radio nuclides, cooling and counting times. The difference between the measured and certified elemental concentrations of the elements (within $\pm$ 7%) can be taken as a measure of the accuracy of the method. The elements namely Fe Co, Ga and Mn are determined by k0 – INAA for which certified values are not available.

Out of the seven key elements of a natural gemstone, five elements namely Fe Al, Mn, Cr and Sc are present in all the four samples. The element K was absent in sample 3 and 4, where as Br was absent in sample 3 (Table1). The concentration of Be couldn't be measured by the present method. However, gemstones are reported to have many elements at trace levels, some of which are value added elements. The results of Alexandrites were compared with that of Chrysoberyl and Chrysoberyl Cat's eye, previously studied by us. It was noticed that the mean concentrations of Al in the three classes are almost same, which is around 40% and is in good agreement with the formula BeO. Al2O3. The Cr concentrations in Chrysoberyl and Chrysoberyl cats eye are same, whereas in Alexandrites, it is higher and thus the apparent greenishness is due to the higher concentration of Cr. Whereas, Fe concentration in Chrysoberyl is higher than Chrysoberyl cats eye and alexandrite. Thus the intense yellow colour of Chrysoberyl is due to higher concentration of Fe. The element Co is present in Alaxandrites, whereas it is absent in other two,. Thus in conclusion, studies on major, minor, trace and rare earth elements will be useful for the distinct geochemical characters of Alexandrites.

Table 1. Elemental Concentration (ppm unless mg/g in indicated) of four Alexandrite Samples.

Element	ALXI	ALX2	ALX3	ALX4
Na	216.9± 5.0	133.9±2.6	161.69±3.99	134.56±2.76
Al*	330±11	403±16	407±19	396±20
K	73.3±13.6	49.88±7.52	ND	ND
Sc	0.59±0.07	0.58±0.04	0.41±0.03	0.63±0.03
Cr*	1.91±0.10	0.92±0.18	3.69±0.21	4.92±0.20
Mn	65.06±1.89	19.70±1.12	112.47±2.70	142.31±2.56
Fe*	21.9±1.4	8.1±0.7	27.4±2.0	36.2±2.1
Co	16.57±0.93	8.39±0.72	46.64±0.45	43.97±1.11
Ca	236.2±3.4	168.6±1.9	205.7±2.0	184.3±1.8
As	0.99±0.15	0.15±0.03	1.63±1.18	2.51±0.81
Br	0.23±0.02	0.13±0.01	ND	0.26±0.02
La	3.19±0.24	2.67±0.17	6.06±0.28	10.64±0.32
Ce	5.77±0.24	5.99±0.83	16.05±0.42	23.56±1.11
Sm	0.43±0.03	0.27±0.01	0.74±0.01	1.66±0.64
Hf	ND	0.65±0.02	1.36±0.06	1.78±0.49
Th	1.55±0.17	1.13±0.16	3.94±0.22	7.15±0.22

Table 2. Elemental Concentrations (ppm unless mg/g is indicated) of IAEA CRM/SL-3.

Element	Measured	Certified	Confidence Interval
Na*	6.67±0.01	6.69	6.29-7.09
Al*	23.9± 0.1	24.5	23.4-25.7
K*	8.89± 0.71	8.74	7.92-9.57
Sc	3.76± 0.07	3.91	3.64-4.18
Cr	40.6 ±1.8	NA	-
Mn	414±6	NA	-
Fe*	11.7±0.6	NA	-
Co	5.39±0.36	NA	-
Ga	6.96±0.34	NA	-
As	3.1±0.1	3.2	3.0-3.4
La	21.3±0.2	22.5	21.6-23.3
Ce	47.2±6.8	45.5	43.9-47.2
Sm	3.87±0.12	3.83	3.53-4.13
Eu	0.67±0.04	0.66	0.64-0.67
Dy	2.06±0.20	2.22	1.65-2.78
Th	6.67±0.28	7.02	6.54-7.50

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Conclusions:

There are many other methods to find out the chemistry or quality of a given material. The polarizing microscope will help in naming a silicate mineral where as an ore microscope or reflecting microscope will help in naming a metallic material with an inference of their chemistry, "which is also qualitative". Every mineral resource will have their own destination for consumption in their respective industry, depending on the nature, quality, quantity and size of the material. When the material is intended for the determination of their chemistry, there are many analytical techniques as described in the earlier chapters. Now the times are fully mechanized and fast pacing. In order to serve the mineral industry as a whole, PIXE is proved to be of the latest utility to fasten the geochemical studies. The present investigation recommends the use of PIXE for fast and reliable results.

In the present investigation a few of the South Indian mineral deposits of precious and semi-precious stone resources of Visakhapatnam District, viz Chrysoberyl, Chrysoberyl cat's eye, Alexandrite and gem garnet are collected from parts of South India and analyzed for the validity and reliability of various instrumental techniques. The gravimetric and titrimetric methods need higher amount of attention by the individual. In the non-destructive analytical techniques, it can determine mass fraction limited to 40 elements. It would be difficult to obtain low detection limits of the samples due to the consideration of their half-lives. It is also difficult to determine some of the transition metals. In the case of XRF analysis, even though it has a wide range of application of geochemical research, it requires relatively large homogeneous samples and needs proportionally highly priced standards. In the case of ICP-MS, it requires precautions of sample solutions and reduction of efficient spectral interferences. In the case of AAS analysis, it has the capacity to determine over 62 different metals in a given solution. Preparation of standard solutions is elaborate. In this perspective, the utilitarian aspect of both INAA and PIXE are studied with reference to a few south Indian minerals to find their acceptability.

The distinction of Chrysoberyl / Chrysoberyl cat's eye and alexandrite is also determined due to the variation of the concentration by the element chromium. Chromium recorded higher concentration up to 4.92% from 0.92% due to the intensity of colour change of mineral from green to red under incandescent light. This forms a major contribution of the present investigation.

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