Original Research Article

FAAS, FT-IR and XRD identification of natural and heat treated opals located in Wadla Woreda, North Wello, Ethiopia

Abstract

Opals are naturally occurring hydrous silica materials (SiO_2*nH_2O), and have been largely used in jewelry and as decorative elements in artworks due to their optical properties. In this study, we present some gemological properties, a combined spectroscopic (FAAS, FTIR) and X-ray powder diffraction (XRD) identification of natural and heat treated opals obtained from the main deposits in North Wollo, Ethiopia. The gemological measurements, FTIR and XRD spectra for natural and heat treated samples are nearly identical, FAAS shows clear differences on their color this may be due to the concentration differences of metals. Both of these opals showed spectra and diffraction patterns typical of Opal-CT, with clearly defined patterns and main peaks in the 2θ range of cristobalite and tridymite, called microcrystalline opals.

Keywords: Opal; XRD; FAAS; FT-IR; Opal-CT; microcrystalline.

1. Introduction

The gemstone exploration has recent history in Ethiopia. There are few studies on Ethiopian gemstones conducted by different researchers. The diverse geology of Ethiopia comprises a Varity of metallic, precious gemstone and industrial mineral [1]. Gemological finding indicates that many parts of Ethiopia are potential sources of precious and semi-precious stones. Studies have so far shown that the following gemstones are found in Ethiopia: Emerald, Apatite, Almadine, Amethyst, Aquamarine, Chalcedony, Citrine, Jasper, Peridot, Topaz, Diamond, Sapphire, Tourmaline and opal [2]. In Ethiopia precious opal is found in tertiary volcanic with in rhyolitic ignimbrite or tuff as concretions that are covered by compacted acidic ash shell with different colored amorphous silica in center. The opal have generally large size and wide range of colors, including clear, translucent, white, yellow, orange, red, blue, green and dark reddish brown [3]. The unique patterns that make it differ from other gem types are their characteristic color depth, shade and the play of pattern [4].

Natural opal is one of the most known and expensive gemstones. Its beauty depends on optical properties. It consists of nanosized marbles of SiO_2 and the pores between the marbles are filled with amorphous glass. Their intensity of light diffracted by a crystal is defined by optical property of spheres (marbles) and pores. However, gem-opals have weak contrast of index of refraction between SiO_2 spheres and pores and it consists of many different micro crystals [5]. The internal colors are produced by ordered silica sphere, these causing the interference and diffraction of light passing through the microstructure of gem-opal. The quality of precious opal can be determined by the regularity of the size and the packing of these spheres [6].

Opal is found in Afar region, Northern Shewa, Northern Wollo and Southern Gondar suggesting that it is a huge belt extending from Eastern to central Ethiopia. The occurrence of precious opal reported in Warder, Ogaden and Dire-Dawa. The precious opal has become an important mineral commodity, because it has satisfactory structural stability, durability, play of color, color saturation and color patterns. Due to these demands, precious opal has become an important mineral. Current price of rough, cut and polished gem-quality Opal is $1450-1600 USD per kilograms [7].

By now, the world already has a taste of the Ethiopian opals. And the little that has so far been known of them, especially their brilliant qualities and abundant “play of color(s)”, have proved irresistible attractions [8]. Therefore, mining operations of gem-opal within the country is expected to be an important economic catalyst for the Government’s export-orientated development strategy. By recognizing the need to promote the market-oriented modern mineral production, processing and marketing system, the Ministry of Mines established Mineral Market and Value Chain Development Directorate in 2014 bestowed with diverse responsibilities [9]. So identification of chemical and physical properties of opals from a particular geographical location is important for several reasons. For example, for the sellers are very useful to know the provenance, as the gems of some localities are more valuable than others. In addition, in the knowledge of the geographical origin is crucial to reconstruct the trade routes of gem [10].

This paper therefore, presents results of the physical properties such as refractive index, specific gravity, and hardness as well as the spectroscopic techniques such as FT-IR, FAAS and XRD that were used to identify and characterize the natural gem-opal hosted in Ethiopia, North Wello, particularly Wadla Woreda. The Wello Province opal which is different from the previous Ethiopian opal is more closely resembled the sedimentary opals of Australia and Brazil, with a light background and often vivid play-of-color. Wello Province opal, more commonly referred to as "Welo" or "Wello" opal has become the dominant Ethiopian opal in the gem trade [11].

2. Experimental

2.1 Chemicals

Opal was collected from North Wello, Ethiopia. All chemicals that were used in the analysis are analytical grade. Nitric acid (70%), hydrochloric acid (35.5%), hydrogen peroxide (30%), and hydrofluoric acid (48%), potassium bromide were obtained from Merck, India. All chemicals were used without further purification. Deionized water was used throughout the experiment.

2.2 Sample location

The sample was located from Amhara National Regional state, North Wello zone, Wadla Woreda localities, which are 649 km far from Addis Ababa which is the capital city of Ethiopia, and 128 kms from the capital city of North Wello zone, Woldia. The other and optional way of direction of the listed woreda is 567 km from Addis Ababa which across through Dessie followed by Kuta Ber Woreda, South Wollo. The woreda is bordered on the southeast by Delanta, on the southwest by Dawunt, on the north by Meket, and on the northeast by Guba Lafto. The major town in Wadla is Kone. The altitude of this woreda ranges from 700 to 3200 meters above sea level. It lies in the watershed of the Bashilo; rivers include the Zhit'a as shown in (**Figure 1**).

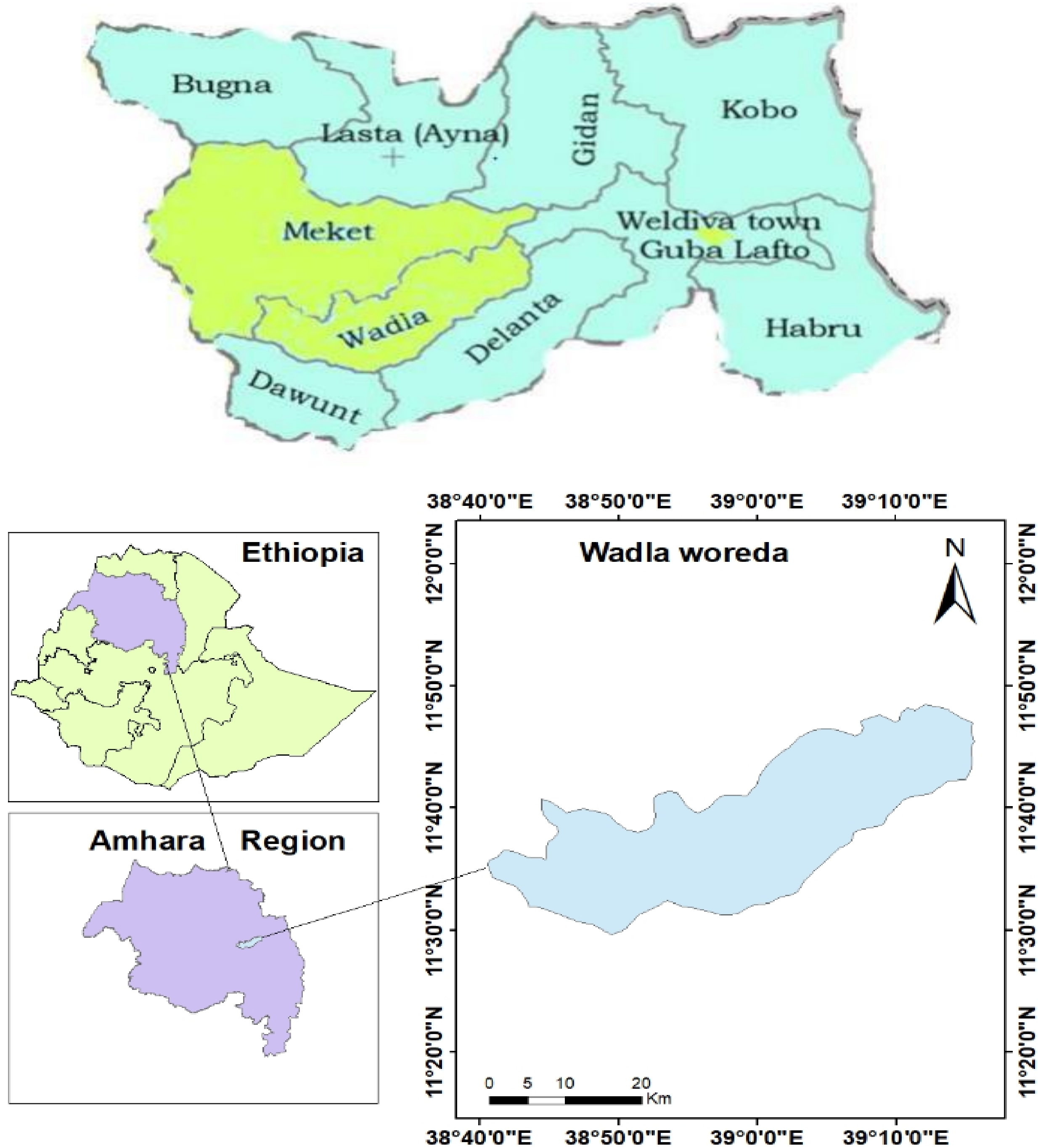

Figure 1: Map of North Wello, Amhara, Ethiopia.

2.3 Sample collection and preparation

The natural opal sample was collected from Wadla Woreda, North Wello Ethiopia. Their body color and shape was described in (**Figure 2a**). In addition, similar natural opal sample was placed in porcelain crucible with cooking sesame oil until all the body of the opal covered with the oil and then simmer the opal stay below boiling point about 4 hr. The opal was regularly checked until a nice shade of black color observed (**Figure 2b**). Then, turn off the heat, allowed to cool in sesame oil and washed with detergent (heat treated opal). The natural opal and heat treated opal samples were washed with deionized water, air dried and crushed using jaw crusher followed by mortar and pestle and finally the powder was sieved with a 0.1 mm size. The powdered samples were kept in a desiccator for further analysis.

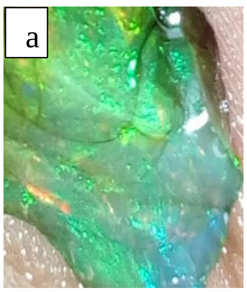

Figure 2: Natural opal (a) and Heat treated opal (b).

2.4 Characterization

2.4.1 Determination of gemological properties

The physical properties of the samples were measured in order to verify that the samples are real opals or not. These gemological (non-destructive) characterization tests were performed on representative samples. The tests were performed at Woldia University department of chemistry laboratory, Woldia. For these purpose a refractometer of UK manufacturer was used to measure refractive index (RI) with an optical contact liquid of 1.78±0.05, RI at room temperature and the specific gravity was measured by heavy liquid method using Lithium salt. The instruments of moh's hardness pencils were used to determine the hardness of the opals.

2.4.2 FAAS determination

FAAS analysis of opal samples were determined according to [[12],[13]]. For FAAS analysis, the powder opal sample (0.5g) was weighed and put in to 50mL borosilicate glass of Erlenmeyer flask and 5mL conc. 69-72% HNO_3, 2mL 35.5% HCl, 1mL 30%w/v H_2O_2 and 2mL of 48%HF were added in to the flask. After the Erlenmeyer flask was heated on hot plate and the solution evaporated near dryness. After that 2 mL 48% HF was added on flask and heated for a few times until precipitation of SiO_2 is eliminated as SiF_4 vapors. Cooling down to the room temperature, 2mL conc. HCl and 5 mL of distilled water were added then filtered through Whatman no. 42 filter paper and diluted to 50 mL volumetric flasks with deionized water . The FTIR analysis was carried out by taking powdered gem-opal sample exactly 2mg (using electronic digital balance) and mixed with 200mg KBr in order to prepare circular pellet. The XRD patterns analysis was carried out by taking powdered natural gem-opal sample and transferred it into sample holder of the instrument [14].

2.4.3 FT-IR determination

The Fourier-Transform Infrared (FT-IR) spectra of the samples were recorded on FT-IR spectrometer (JASCO model 4100) using KBr method. The FTIR analysis was carried out by taking powdered opal samples exactly 2mg (using electronic digital balance) and mixed with 200mg KBr in order to prepare circular pellet and then the spectra were recorded in the range of 4000-400 cm^{-1}.

2.4.4 XRD determination

The crystalline nature of natural opal and heat treated opal were studied by powder XRD using graphite monocromatized Cu Kα radiation. The XRD patterns analysis were carried out by taking powdered opal samples and transferred it into sample holder of the instrument [15] with a range of 2θ of 10-70°.

3. Result and discussion

3.1 Gemological properties

To verify that the investigated rough gem-opal samples were indeed opals, non-destructive gemological characterization tests were performed on representative samples. The gemological properties of opal samples from North Wello, Ethiopia were given below in (**Table 1**): the hardness, refractive index and specific gravity values are comparable with reported literatures in [16, 17, 18, 19, 20].

Table 1: Gemological properties of natural and heat treated opal.

Gemological measurements	Natural opal	Heat treated opal
Hardness	5.80	6.00
Refractive index	1.46	1.44
Specific gravity	2.12	2.05

In the visible spectrum, as shown in (**Figure 2)** their body color has yellow, orange, red, white, brown and blue for natural opal and their body color has black, white and brown for heat treated opal. Results of all these gemological testing values indicate that the sample is indeed opal [21].

3.2 Flame Atomic Absorption Spectroscopy (FAAS) determination

The content of trace elements determined using FAAS of the investigated opals were presented in (**Table 2**). As seen from the table: Zn, Pb and Cu were the most abundant whereas the concentration of other elements were very small. The body color of opals (when it could be established) has so far always been linked to inclusions [22]. Some elements are usual implication for coloration (pigmenting agent) and genesis. The content of different trace elements; (Mg, Zn, Cu, Pb and Mn) was analyzed by Flame Atomic Absorption Spectroscopy (FAAS) technique. The results of the measured values were in agreement with literature data which verify that the samples were indeed opals. The metals level observed in both samples are comparable with their corresponding worldwide reported values [23]. Color variation of the two opals were formed due to the concentration difference of metals presented.

Table 2: Mean concentration (mg/g) of trace elements in natural and heat treated opals.

Sample type	Metals Av. Conc in mg/g				
	Mn	Mg	Zn	Pb	Cu
Natural opal	0.056	0.326	3.521	0.833	0.623
Heat treated opal	Negligible	0.280	0.415	0.985	0.129

As shown (**Figure 3**) below, the effect of heat on the nature as well as nutrient availability on the given opal. As the heat varied, the elemental composition also varry. This indicated how heat influnces the elemental composition of natural opal. Before heat treated the elemental zinc was high while Lead element becomes low. But after heat applied zinc element minimized while lead maximized. This indicated that every element has their own character with regards to heat reactivity or sensitivity [24].

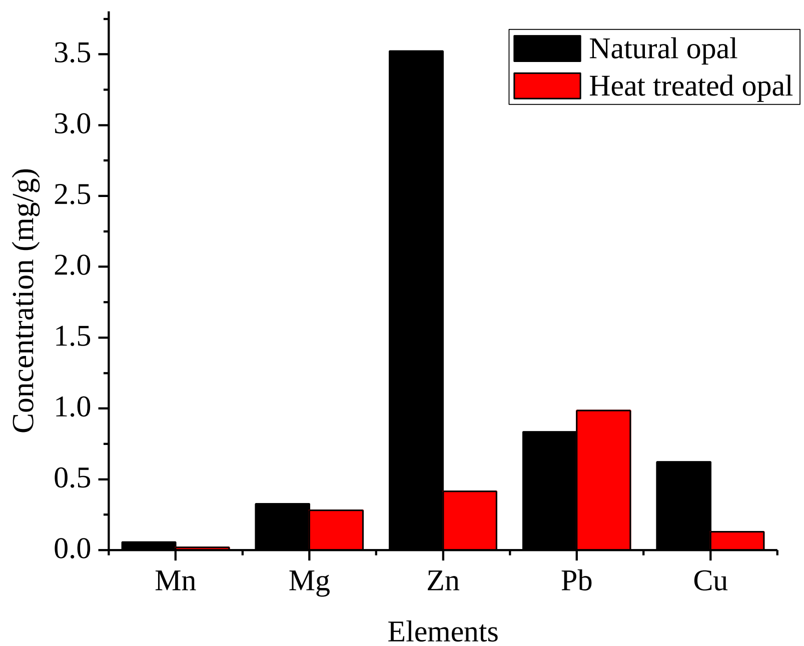

Figure 3: the elemental composition of natural and heat treated opal.

3.3 Fourier Transform Infrared Spectroscopic (FT-IR) analysis

The infrared absorption measurements were performed by the KBr micro pellet method, using Fourier transformed IR spectrometer and the spectra were recorded in the range of 4000-400 cm^{-1} described in (**Figure 4**). All IR spectra/absorption bands for both natural and heat treated opals were appeared almost in similar regions and absolutely compatible with those already available in the literature. Broad band absorptions at about 3445 cm^{-1} are due to the O-H stretching vibrations of hydrogen bonded molecular water and SiOH group (silanol). A weak absorption peak at about 1632 cm^{-1} are due to the presence of molecular water (H-O-H) bending vibrations [**25, 26**]. Three peaks in the low frequency region of 2000-400 cm^{-1}, at around 1100, 795, and 475 are because of the absorptions of the silicate stretching vibrations [27, 28]. The absorbance/absorption intensity of heat treated opal was lower than natural opal, due to dehydration and polymerization of surface silanol and transformation of network structure may occur simultaneously via the effect of heat [29].

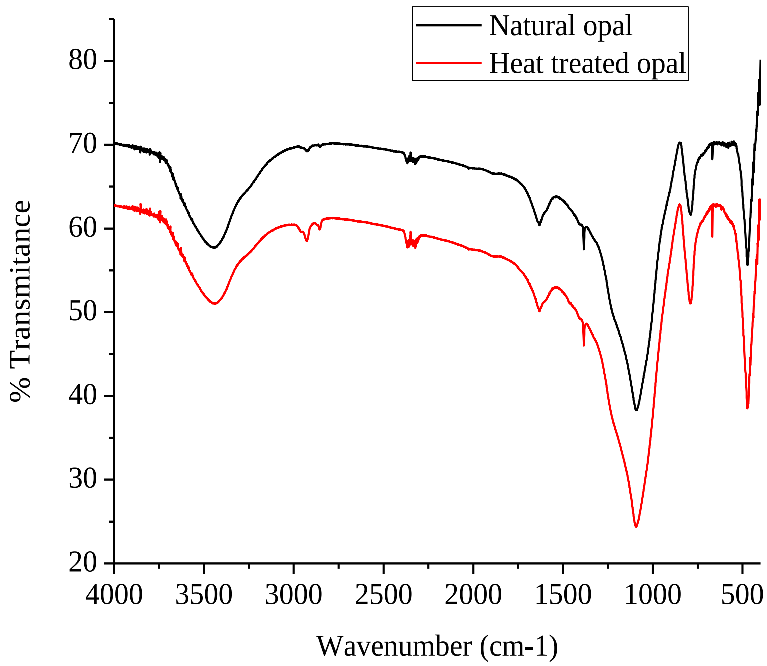

Figure 4: FT-IR spectra of natural and heat treated opals.

3.4 XRD determination

X-ray powder diffraction data were obtained using powder diffractometer working with graphite monocromatized Cu Kα radiation in the range 2θ, 10-70°. The X-ray powder diffraction analyses performed are able to classify opals in to their common groups such as opal-A, opal-C and opal-CT [25, 30]. XRD patterns for natural and heat treated opals are shown in (**Figure 5**). The position of diffraction peaks for natural opal is very similar to that of heat treated opal. Both opal samples showing well resolved peaks at 21.67º, 35.84º, 44.52º, and 56.96º are considered as opal-CT according to [27] classification.

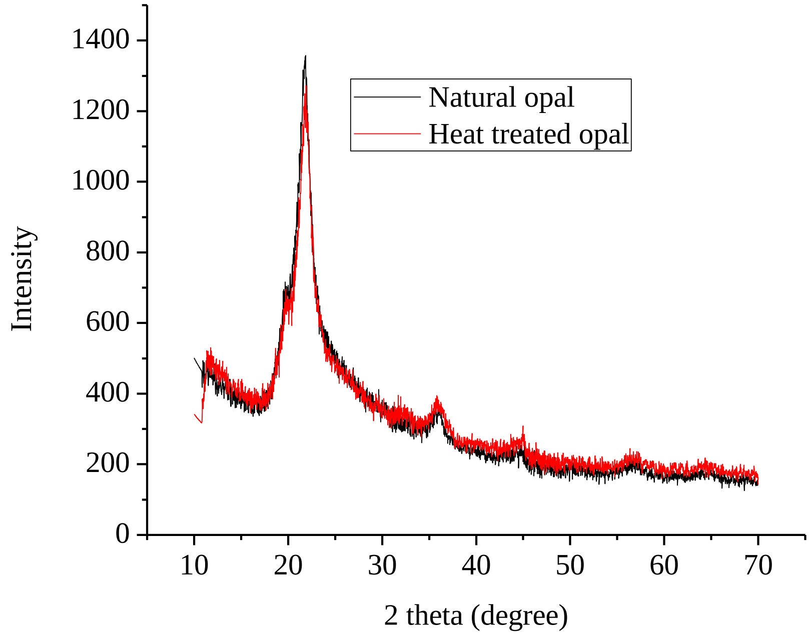

Figure 5. The XRD pattern of natural and synthetic opals.

4. Conclusion

Opals are water-bearing micro- to non-crystalline materials, composed of micro-spheres of hydrated silica (SiO_2*nH_2O) and differ in the crystallinity degree/crystal-structure arrangement. On the basis of their mineralogical composition, it can be classified in to opal-C: a well-ordered form, consisting predominantly of α-cristobalite; opal-CT: semi-crystalline, consists of crystalline regions of α-cristobalite and α-tridymite; and finally opal-A: the most disordered typology, predominantly amorphous and corresponds to the most disordered structure. In this work, the gemological measurements and FAAS determination clearly shows that samples are indeed opals. The application of FT-IR is essential for functional group identification and the structural characterization of microcrystalline opals known as Opal-CT, cristobalite and tridymite like structural species analyzed by XRD.

Availability of data and materials

All data generated or analyzed during this study are included with in the body of the manuscript.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

Reference

1. Senior, B. R." Weathered-profile-hosted precious opal deposits."*AGSO Journal of Australian Geology and Geophysics* 17 (1998): 225-228.
2. Yager, T.R. The Mineral Industry of Ethiopia. U.S. Geological Survey Minerals Year Book 2007. Ethiopia [Advance Release]. (2009).
3. Stewart, A. M., Lewis T. Chadderton, and Brian R. Senior. "Self-assembly in the growth of precious opal." *Journal of Crystal Growth* 312, no. 3 (2010): 391-396.
4. https://www.opalauctions.com/learn/opal-information/opals-of-the-world. (Accessed on Monday, April 04, 2017, 4:12:47 AM).
5. Olga Kavtreva "Structural characterization of photonic crystals based on synthetic and natural opals" Seminar: July 19, 2005.

6. Fedotova, Maria. "Diamonds as the Alternative Assets on Financial Markets." Master' thesis, 2014

7. Amhara National Regional State Education and training development Agency (Bahirdar, Ethiopia). Stone makes human being to exist as a human being (Amharic version) (Pamphlet).

8. Geological survey Ethiopia; https://ethiopiaobservatory.com/2013/04/23/ who-Is benefitting from-Ethiopia-global-brand name-opals/ Accessed on Wednesday, April 01, 2017, 9:12:47 PM.

9. U.S. Department of the Interior (2016) U.S. Geological Survey ETHIOPIA: 2013 Minerals Yearbook http:// minerals. Use. gov/ minerals /pubs/ country/ 2013/ myb3-2013-et.pdf.

10. Smallwood, A. G., P. Thomas, and A. S. Ray. "Comparative analysis of sedimentary and volcanic precious opals from Australia." *Journal of Australasian Ceramic Society* (2008).

11. Choudhary, Gagan, and Rajneesh Bhandari. "A new type of synthetic fire opal: Mexifire. "*Gems & Gemology* 44, no. 3 (2008):228-233.

12. Makreski, Petre, Gligor Jovanovski, Trajče Stafilov, and Blazo Boev. "Minerals from Macedonia XII. The dependence of quartz and oral color on trace element compositionAAS, FT IR and MICRO-RAMAN spectroscopy study." *Bulletin of the Chemists and Technologists of Macedonia* 23, no. 2 (2004):171-1

13. Yenus Abubeker and Walelign Wubet, Identification and Spectroscopic Characterization of Natural Gem Agate from West Belessa, North Gondar, Ethiopia, 2017.

14. Woldesenbet Bafe Dilabo, Walelign Wubet Melkamu; spectroscopic studies on natural Gem opal hosted in Ethiopia: South Gonder. (Final thesis)

15. Woldesenbet Bafe Dilabo, Walelign Wubet Melkamu; spectroscopic studies on natural Gem opal hosted in Ethiopia: South Gonder. (Final thesis)

16 . https://en. .wikipedi. webmineral.com, Opal [accessed, 8:12, 1/4/2009 E.c].

17. Choudhary, Gagan, and Rajneesh Bhandari. "A new type of synthetic fire opal: Mexifire."*Gems & Gemology* (2008): 44, no. 3, 228-233.

18. Caucia, Franca, Luigi Marinoni, Christian Ghisoli, and Alberto Leone. "Gemological, physical and chemical properties of prase opals from Hanety Hill (Tanzania)." *PERIODICO DI MINERALOGIA* 85, no. 1 (2016): 41-50.

19. Caucia, Franca, Luigi Marinoni, Alberto Leone, and Ilaria Adamo. "Investigation on the gemological, physical and compositional properties of some opals from Slovakia (“Hungarian” opals)." *Periodico di Mineralogia* 82, no. 2 (2013): 251-261.

20. Hatipoglu, Murat, Yasar Kibici, Gursel Yanik, Cafer Ozkul, Mehmet Demirbilek, and Yasemin Yardimci."Nano-structure of the Cristobalite and Tridymite Stacking Sequences in the Common Purple Opal from the Gevrekseydi Deposit, SeyitömerKütahya, Turkey" 31, No. 1 (2015): 35-49.

21. Hatipoğlu, Murat. "Moganite and quartz inclusions in the nano-structured Anatolian fire opals from Turkey." *Journal of African Earth Sciences* 54, no. 1 (2009): 1-21

22. Gaillou, Eloïse, Aurélien Delaunay, Benjamin Rondeau, Martine Bouhnik-le-Coz, Emmanuel Fritsch, Guy Cornen, and Christophe Monnier. "The geochemistry of gem opals as evidence of their origin." *Ore Geology Reviews* 34, no. 1 (2008): 113-126.

23. Tadesse, J.-P. Milesi and Y. Deschamps, *Elsevier Journal of African Earth Sciences* **2003**, *36*, 273-313.

24. Olga Kavtreva "Structural characterization of photonic crystals based on synthetic and natural opals" Seminar: July 19, 2005.

25 . Ilaria Adamo, Christian Ghisoli, and Franca Caucia**.** A contribution to the study of FTIR spectra of opals. N. Jb. Miner. Abh. March 2010. 187/1, 63–68

26 . *Alver et al. / Anadolu Univ. J. of Sci. and Technology – A – Appl. Sci. and Eng. 17 (5) - 2016*

27. A. Sodo, A. Casanova Municchia, S. Barucca, F. Bellatreccia,a G. Della Ventura, F. Butinib and M. A. Ricci, Raman, FT-IR and XRD investigation of natural opals. 27 May 2016

28 . M. Hernández-Ortiz, G. Hernández-Padrón, R. Bernal, C. Cruz-Vázquez, V. M. Castaño. Nanocrystalline mimetic opals: synthesis and comparative characterization vs. natural stones. *International Journal of Basic and Applied Sciences, 4 (2) (2015) 238-243*

29. A Inoue *et al* 2010 . Shock compression of synthetic opal; *J. Phys.: Conf. Ser.* **215** 012147

30. **Neville J. Curtis , Jason R. Gascooke , Martin R. Johnston and Allan Pring.** A Review of the Classification of Opal with Reference to Recent New Localities. *Minerals* **2019**, *9*, 299