

# Chemical Composition Analysis on Amethyst

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## Abstract

Amethyst is one of the most popular ornaments in Chinese culture. Here, aiming at clarifying the component of amethyst, chemical analysis by energy dispersive X-ray spectrum and powder X-ray diffraction, combined with Raman and infrared absorption spectrum, was carried out. Energy dispersive X-ray spectrum suggested that its dominant elements is silicon and oxygen in the atomic concentration ratio of 18.98:43.01, with tiny iron, cobalt or manganese in the mass percentage less than 1%. Further, X-ray diffraction demonstrated that its main phase is crystalline quartz, with the transition metals embedded in the crystal lattice, and the conclusion of which was also confirmed by lattice dynamics analysis based on Raman and infrared absorption spectra. Through our study, the component of amethyst was clarified.

*Keywords: Amethyst; Chemical Composition; Crystal Structure; Quartz*

## 1. Introduction

In Chinese traditional culture, purple symbolizes nobility, elegance, happiness and peace, and amethyst is one of the most popular ornaments in the living and office room in China (Ye, 1994). In our living room there is an amethyst hole. The question about the component of amethyst has been interesting to me, since my dad bought the amethyst hole and placed it there seven years ago.

This query has been asked to many people around, and the gotten answers covered from crystal glass, gemstones, diamond to even jade, etc. To clarify these controversies and get an academic response, a comprehensive literature research was implemented. Accordingly, in these previous studies, by X-ray diffraction, the main phase of amethyst was indexed to be quartz ( $\text{SiO}_2$ ) with a small amount of defect (Wu, 2016 and Suastika 2017). However, the deviation of crystal structure from pure quartz induced by the defects, has never been concerned, and the exact lattice constant of amethyst is still unclear. Besides, pure quartz is colorless, and it is anticipated that the purple color is attributed to the optical absorption from the defects. By utilizing absorption spectra, the defects, that give rise to the purple color, was indirectly assigned to the tiny iron atoms and some other transition element (Liu, 2022). It should be noted that absorption spectrum is an indirect element analysis approach. The direct evidence that strongly support the origin of the purple in amethyst is still inadequate. The objective of this study is to disclose the exact chemical composition in amethyst. According to literature review, it is anticipated the main component is quartz ( $\text{SiO}_2$ ) in a high probability, and here the exact defect



**Figure 1** The amethyst ornament in our living room. The inset displays the part used for chemical component analysis.

element, that result in the purple color, will be explicitly determined. Moreover, the values of lattice constant modified by the defect will be refined as well. Here, for this purpose, a small piece was cut from the ornament, and element analysis and atomic arrangement determination is carried out on it.

## 2. Materials and Methods

### 2.1 Sample Preparation

The amethyst cut from the ornament was firstly soaked by dilute nitric acid for 24 hours to dissolved the impurity in the surface, and then washed by deionized water. After being kept in drying oven for 6 hours to remove the surface water, by an agate mortar the amethyst was well grinded in to powder. The powder sample was used for all the measurement.

### 2.2 Chemical Element Analysis

Chemical element analysis on amethyst was performed by the method of energy dispersive X-ray spectroscopy (EDX), implemented by a Hitachi S4800 scanning electron microscopy. Under the electron beam irradiation, X-ray is emitted from the constituent atoms in the sample. The elements and corresponding contents can be determined from the characteristic energy and intensity of the emitted X-ray (Zieba, 2000).

### 2.3 Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) data is an effective tool to determine microscopic structure in atomic scale. It was collected by a PXRD apparatus of Rigaku smartlab SE, with a Cu K $\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ). The  $2\theta$  range was set to  $5^\circ \sim 90^\circ$  with the scanning angular step of  $0.02^\circ$ , and the scanning rate was set to a slow value of  $0.2\text{s/step}$  to guarantee a high intensity, so as to make the tiny components in the sample show up. The angles of diffraction peaks are different from one component to another in PXRD spectrum, and according to the angles where diffraction peaks occur, the components in the sample can be identified (Gualtieri, 1997). JADE 6.0 was employed to index the PXRD spectrum. The PXRD spectrum was refined by FULLPROF Suit (Rodriguez-Carvajal, 2008).

### 2.4 Raman and Infrared Absorption Spectrum

The atomic type and arrangement can also be reflected in the atomic vibrational frequency, which can be studied by Raman and infrared absorption spectrum. Raman spectrum was collected by a LabRAM Aramis confocal Raman spectroscopy system (Renishaw, Invia Raman microscope). A 532nm laser serves as the excitation wavelength, and the spectrum was collected in the range of  $100 \sim 4000\text{cm}^{-1}$ , with the interval of  $1\text{cm}^{-1}$ . The spectrum was integrated for five times to improve the signal-to-noise ratio. Infrared spectrum was recorded by a Thermo Nicolet 6700 infrared spectrometer in the range of  $400\sim 4000\text{cm}^{-1}$  with a spectral resolution of  $0.5\text{cm}^{-1}$ . In the infrared absorption measurement, a flake tableted by mixture of powder amethyst and KBr in the mass ratio 1:99 was used. The peaks in Raman and infrared absorption spectrum characterize the atomic vibrational frequency in the sample, by which the types of the constituent atomic unit can be identified.

## 3. Results and Discussion

In order to determine the chemical composition, it is prerequisite to identify the constituent elements in amethyst. Energy dispersive X-ray spectrum performed by scanning electron microscopy, which distinguish the element via the emitted X-ray under electron radiation, tells that silicon, oxygen, iron, cobalt and manganese elements are included in the sample. As displayed in Table 1, the quantitative analysis unveils that silicon and oxygen dominantly occur in the sample, with the mass percentage of  $\sim 99\%$ , and those of transition metals, *i.e.*, iron, cobalt and manganese, are less

than 1%. Remarkably, the atomic concentration ratio between silicon and oxygen are 18.98:43.01, which is close to 1:2 by considering the measured error. This suggests that the main phase of amethyst is quartz ( $\text{SiO}_2$ ), and iron, cobalt and manganese may exist in the form of impurity. It should be emphasized that, conventionally, the pure quartz is colorless and absolutely transparent. It is speculated that the purple of amethyst may arise from the light absorption of the constituent transition metal elements (Marzouk, 2006), and the uneven distribution of purple is attributed to their distribution inhomogeneity in the main phase of quartz (Figure 1).

**Table 1** Element analysis result of energy dispersive X-ray spectrum

Element	Concentration(a.u.)	weight%
O	43.01(32)	55.93(42)
Si	18.98(26)	43.19(59)
Fe	0.15(8)	0.68(36)
Co	0.04(9)	0.19(43)
Mn	0.00(16)	0.00(71)
Total		100.00

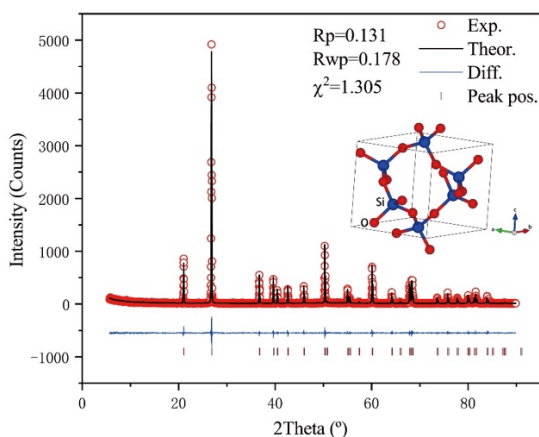


Figure 2. Powder X-ray diffraction spectrum of amethyst.  $R_p$ ,  $R_{wp}$  and  $\chi^2$  are the profile R-factor, weighted profile R-factor, and goodness-of-fit for the refinement, respectively. Red circles and black line are the experimental and theoretical XRD spectra respectively, blue line is the difference between the experimental and theoretical spectra, and red bars indicate the theoretical peak positions.

Powder X-ray diffraction (PXRD) can distinguish whether a solid is in crystalline- or non-crystalline states, via sharp diffraction peaks or broad scattering bump occurring in the spectrum. If it is the former, the chemical composition can be determined by the angles where the diffraction peaks emerge. Accordingly, sharp peaks are observed in the spectrum, and a smooth scattering background without bump is manifested, as plotted in Figure 2. This demonstrates that the compositions are all crystalline and no non-crystalline is included. All the diffraction peaks can be indexed to the quartz in the space group  $P3_22_1$  with two independent cell parameters  $a=4.913\text{Å}$  and  $c=5.405\text{Å}$  (PDF card No. 99-0088, Le Page, 1976). Moreover, except the diffraction peaks belonging to quartz, no peaks, that are indexed to the compounds containing iron, cobalt or manganese, are detected. This demonstrates that these transition elements are embedded in the crystalline lattice of quartz, but do not exist in the form of isolated compounds. The cell parameters are refined to be  $a=4.92068(3)\text{Å}$  and  $c=5.41291(6)\text{Å}$  on the PXRD spectrum, which agree with

the values in standard PDF card. The slight deviation between the theoretical and refined values may be due to the doping of transition metals with the different atomic radii from silicon and oxygen atoms.

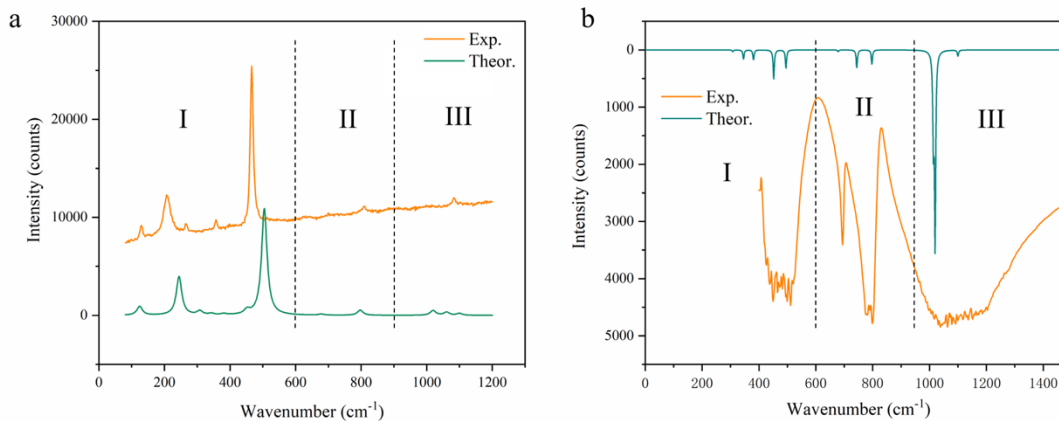


Figure 3. Raman (a) and infrared (b) absorption spectrum of amethyst

To further confirm the composition determined by energy dispersive X-ray spectroscopy and powder X-ray diffraction, the atomic vibration spectrum analysis based on Raman and infrared absorption spectrum are implemented. Raman and infrared absorption spectrum are two sets of complementary approach to investigate the intrinsic atomic vibrational frequency and the corresponding intensity, by which all the atomic vibrational frequency can be detected (Dove, 1993). As displayed in Figure 3, both the Raman and infrared absorption spectrum are consistent with those measured by Briggs and Soda respectively (Briggs, 1977; Soda, 1961). Roughly, these peaks can be divided to three types: (I) those below  $\sim 600\text{cm}^{-1}$  are attributed to the atomic vibration of the whole skeleton as a quasi-rigid unit; (II) The vibration of the silica structure, i.e., the twisting and rotating of the  $\text{SiO}_4$  units predominantly account for the peaks between  $\sim 600\text{cm}^{-1}$  and  $900\text{cm}^{-1}$ ; (III) Remarkably, a peak is detected at  $\sim 1100\text{cm}^{-1}$ . The previous study performed by Tekippe et al has explicitly disclose that this Raman peak directly characterize the stretching vibration of Si-O bonds in quartz (Tekippe, 1973). All these observation in Raman and infrared spectrum confirm that the main phase of amethyst is quartz.

#### 4. Conclusion

In summary, to disclose the composition of amethyst, the energy dispersive X-Ray spectrum, powder X-ray diffraction, Raman and infrared absorption spectrum was performed. Energy dispersive X-ray spectrum suggests that its main component is quartz with tiny (less than 1%) transition metal, including iron, cobalt and manganese. By powder X-ray diffraction, it is demonstrated that amethyst has a crystalline state, and can be indexed to quartz. The slight deviation between the refined and theoretical values of the lattice constants verifies the dopant of iron, cobalt and manganese with the different radii from silicon and oxygen atoms. Further, the conclusion that main component is quartz, is confirmed by atomic vibration analysis based on Raman and infrared absorption spectrum analysis. Our study answers the question what is the exact composition amethyst, and clarifies that amethyst is quartz with tiny impurity of iron, cobalt and manganese inserted in the crystal lattice.

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