Short Communication

Structural study of the metamict states by X-ray diffraction: In the case of naegite

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Abstract

A structural study of the metamict zircon "naegite" has been carried out by obtaining radial distribution function (RDF) from measured X-ray scattering intensity data. Structural parameters of interatomic distances and coordination numbers were estimated from the RDF data using the pair function method. The silicon atom was found to occupy a tetrahedral site of oxygen. The structural parameters of first neighbouring Zr-O pair agree well with those of crystalline zircon, although the slight decrease in its interatomic distance is detected. Since the correlation of the cation-cation pairs around 0.30 and 0.36nm are well attributed to those of the crystalline zircon, the metamict zircon is considered to have similar short range order as that found in the structure of crystalline zircon.

Introduction

The minerals produced in the metamict condition have received much attention in many years, since the detailed discussion including history and description of the word "metamict" was provided by Pabst (1952). These materials mostly contain radioactive elements such as U and Th, whose radioactivity is considered to be one of the main origins for the metamictization (e.g. Ewing, 1975). Recently, the structural study of self-irradiation damage of metamict materials is of great interest in radioactive waste science, therefore the structural characterization of the naturally occurring metamict minerals is no longer considered as a mineralogical curiosity (Roy and Vance, 1981). However, several metamict minerals lack internal order and are amorphous to X-rays, which causes a serious obstacle to clarify the structural features of these mineral species and only a small number of structural investigations (Keller and Wagner, 1983; Nakai *et al.*, 1987)

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have been carried out so far. Therefore the structural features of the metamict minerals or metamictization have not been fully revealed yet.

Among a number of metamict minerals, metamict zircon “naegite” is a zirconium silicate containing rare earth and radioactive elements such as Y, U and Th. Nakai *et al.* (1987) reported the environment around a zirconium atom in naegite by means of the extended X-ray absorption fine structure (EXAFS) method and suggested the decrease in the distance and coordination number for Zr-O pair, although some reservations are stressed regarding the quantitative accuracy of their absolute values due to the experimental and theoretical difficulties of the EXAFS method. The main purpose of this paper is to provide structural parameters in the first nearest neighbor region relevant to a silicon and a zirconium atom in naegite by determining the radial distribution function obtained directly from a X-ray diffraction profile.

Experimental Procedure

The natural specimen used in this study was metamict zircon “naegite” from Naegi, Gifu Prefecture, Japan. Naegite is a variety of zircon: $(\text{Zr,Hf})\text{SiO}_4$ which is rich in Y, Nb, Ta, Th and U and always in the metamict state (Nagashima and Nagashima, 1960). The chemical composition of naegite from this locality has been reported to be: 30.0wt% SiO_2 , 48.7% ZrO_2 , 3.5% HfO_2 , 2.5% UO_2 , 2.5% $(\text{Nb, Ta})_2\text{O}_5$, 6.1% Ln_2O_3 , 2.9% ThO_2 , 1.4% Fe_2O_3 and 2.7% H_2O (analysed by Kimura cited in the reference Nagashima and Nagashima, 1960). The density, as measured by the Archimedes method with toluene, was 4.09Mg/m^3 , which agrees well with the reported value. Samples of naegite were crushed in an agate mortar and formed into a pellet with a shape of 12mm in diameter and 0.5mm in thickness.

A molybdenum X-ray rotating anode target operated at 50KV and 150mA, and a germanium (111) flat single crystal monochromator in the incident beam were used to measure the intensity data on a ω - 2θ goniometer. An energy sensitive solid state detector was employed to overcome a difficulty arising from the mixing of fluorescent radiations from various elements in the sample. The intensity profile was obtained from $\theta = 3^\circ$ to 60° , which corresponds to the wave vector $Q = 4\pi \sin \theta / \lambda$ from 9 to 153nm^{-1} , where λ is the wavelength and 2θ is the angle between the incident and scattering beams.

Data Processing

The description of the atomic scale structure of disordered systems usually employs the radial distribution function (RDF) defined by considering a spherical shell of radius r centered on an origin atom. The principles of the RDF and their usefulness have been discussed in detail previously (e.g. Klug and Alexander, 1979). Thus only the essential

equations and their relevance regarding data analysis are given below.

For structural study of disordered system containing more than one kind of atom, the concept of unit of composition hereafter designated by uc is frequently introduced (Mozzi and Warren, 1969). In the present case, the feasible unit is approximated to be one zirconium, one silicon and four oxygen atoms for naegite. Then, a reduced interference function, $i(Q)$, is related to the structurally sensitive part of the directly obtained X-ray scattering intensity per uc, I_{eu} . It is defined by the following form;

$$i(Q) = [I_{eu}(Q) - \sum_{uc} f_j^2] / f_e^2 \quad (1)$$

where f_j and $f_e = (\sum_{uc} f_j) / (\sum_{uc} Z_j)$, are the usual atomic scattering factor and the average scattering factor per electron, respectively. The interference function is converted to the radial density function $\rho_j(r)$, which is the electron distribution around a j -th atom at a radial distance of r ;

$$Qi(Q) = 4\pi \int_0^\infty \sum_{uc} K_j r [\rho_j(r) - \rho_e] \sin Qr \, dr \quad (2)$$

where ρ_e is the average number density of electrons and K_j is the effective electron number of species j defined by $K_j = f_j / f_e$ which approximately equals to the atomic number Z_j . Using Eqs.(1) and (2), the following well-known relation is given;

$$4\pi r^2 \sum_{uc} K_j \rho_j(r) = 4\pi r^2 \rho_e \sum_{uc} K_j + \frac{2r}{\pi} \int_0^\infty Qi(Q) \sin Qr \, dQ \quad (3)$$

It is very convenient to introduce a set of pair functions in order to interpret the RDF data, as suggested by Mozzi and Warren (1969);

$$\begin{aligned} \sum_{uc} \sum_i \frac{N_{ij}}{r_{ij}} \int_0^{Q_{max}} \frac{f_i f_j}{f_e f_e} e^{-\alpha^2 Q^2} \sin Qr_{ij} \sin Qr \, dQ \\ = 2\pi^2 r \rho_e \sum_{uc} Z_j + \int_0^{Q_{max}} Qi(Q) e^{-\alpha^2 Q^2} \sin Qr \, dQ \end{aligned} \quad (4)$$

where r_{ij} and N_{ij} are the distance and its coordination number of i - j pairs, respectively. The left-hand side of Eq.(4) provides the theoretical RDF, whereas the right-hand side of Eq.(4) corresponds to the experimental RDF data. The term of $\exp[-\alpha^2 Q^2]$ in Eq.(4) is a convergence factor. This artificial parameter α is zero in the calculation of the experimental RDF using Eq.(4), although this value does not have to be critically selected. On the other hand, the theoretical RDF is calculated using a value of $\alpha = 0.07$. The values of r_{ij} and N_{ij} for the near neighbor region were estimated by a least-squares analysis, so as to fit the experimental RDF. In all computations, the atomic scattering factors with anomalous dispersion terms and Compton scattering factors were taken from the values given in the International Tables for X-ray Crystallography Vol. IV (1974) and Cromer (1969) respectively.

Results and Discussion

Fig. 1(a) shows the X-ray scattering pattern of naegite. It may be worth mentioning that a pronounced shoulder appears at both lower and higher sides of the first main peak and the relatively sharp second peak follows at about $Q=40\text{nm}^{-1}$. As shown in Fig. 1(a), many broad spikes were also found by superimposing the diffuse profile. These peaks can be attributed to those of a crystalline zircon as shown in Fig. 1(b), and thus the similar structural features to those of crystalline zircon may be suggested in this specimen presently investigated. These Debye-like spikes are characteristic of naegite whose original structure is suggested to have been disrupted by the radiation damage of the constituent radioactive elements. Therefore, we tried the following Fourier analysis on the basis of the directly obtained X-ray diffraction profile without any artificial correction.

The interference function $Q_i(Q)$ for naegite is shown in Fig. 2. The profile of $Q_i(Q)$ is composed of the first peak at about $Q=20\text{nm}^{-1}$ followed by a number of well-resolved peaks, which contrasts to the metallic glass cases where the damping behaviour of the function $Q_i(Q)$ is rapid and monotonic. Therefore the oscillations observed in this metamict material imply that a considerable fraction of the local ordering unit

FIG. 1. X-ray diffraction pattern for naegite (a) and crystalline zircon (b).

FIG. 2. Interference function, $Q_i(Q)$ for naegite.

structure such as a SiO_4 tetrahedron is quite feasible, which is given below.

In order to obtain an insight into the structural aspects of naegite, the electron RDF was calculated from the interference function by using the right hand side of Eq.(4) and the resultant RDF is given in Fig. 3. The small oscillations which appear at the lower r side of the first peak around 0.16nm are spurious, considering the ionic radii of the constituent elements. A general ripple with a period of 0.05nm appears to be also detected so as to be superimposed on the original RDF data. A detailed description about the spurious ripples in RDF arising from various origins is given by Furukawa (1962). Following these results, this ripple is found not to originate in the Debye-like spikes.

The arrows in this figure denote the distances of some expected atomic pairs based on the structure of the crystalline zircon: ZrSiO_4 (Hazen and Finger, 1979). The well-resolved first and second peaks in the RDF can be interpreted as the correlations of Si-O and Zr-O pairs, respectively. The atomic distribution of the crystalline zircon enables us to provide the suggestion that the third peak is attributed to the second neighbouring Zr-O and O-O pair. Moreover the fourth peak indicates the contribution of the Zr-Si pair and the fifth peak is related to the Si-Si, second neighbouring Zr-Si and Zr-Zr pairs. They surprisingly well agree with the interatomic correlations found in the structure of the crystalline zircon. Considering these facts, interatomic distances and coordination numbers were estimated by the pair function method using Eq.(4). The dotted line of Fig. 3 is the sum of the first four pair functions for Si-O, Zr-O, O-O and Zr-Si, where the third peak is supposed to be a O-O interaction. The resultant structural parameters

FIG. 3. Electron radial distribution function (RDF) for naegite. The solid line is the measured curve and the dotted line is the sum of the first four pair functions. The arrows indicate the atomic pairs found in the structure of the crystalline zircon.

concerned with the local ordering structure in naegite are summarized in Table 1. These structural information of naegite is consistent with those of the EXAFS results reported by Nakai *et al.* (1987). Therefore it is suggested that the metamict zircon has a similar short range order as that found in the structure of crystalline zircon. However, the following remarks may be worthy of note. Considering the tetrahedral coordination of oxygen around Si and Zr atoms at the first neighbor region, the extremely short distance and large coordination number of the O-O pair obtained in this analysis are not sufficiently enough to be well-approved. This clearly implies that this third peak may be likely interpreted by the mixed correlations of the second neighbouring Zr-O or several O-O pairs which appear in the structure of crystalline zircon. The contribution from other pairs such as Y-O, U-O and Th-O., which are ignored in this RDF analysis, may also be included in this third peak.

For more detailed understanding of the metamict states of naegite and other metamict

TABLE 1. Structural parameters of the near neighbor correlations determined by the use of the pair function method.

i-j pair	Naegite		Crystalline zircon		
	r(nm)	N(atom)	r(nm)	N(atom)	
Si-O	0.164	4.1	Si-O	0.162	4.0
Zr-O	0.209	4.1	Zr-O(1st)	0.213	4.0
			Zr-O(2nd)	0.227	4.0
			O-O	0.249	2.0
(O-O)	0.249	12.0	O-O	0.275	2.0
			O-O	0.285	4.0
Zr-Si	0.299	1.9	Zr-Si	0.299	2.0

minerals, further systematic structural studies are required; for example the environment around a specific element should be determined by modern techniques such as the anomalous X-ray scattering (AXS) method (Waseda, 1984).

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