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Diffraction analysis of metamict samarskite

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Abstract

Samarskite, a chemically complex Nb,Ta oxide with high contents of U and Th has been considered X-ray amorphous. So far, detailed structural information has been deduced from crystallized reaction products after the mineral has undergone heat treatment up to 1000°C. In this study, untreated (neither thermal nor physical) samarskite from Mitchell County, N.C. with a composition approximated by AB_2O_6 where A ions are Y, U and rare earths and B ions are Nb, Ta and Fe, has been investigated by large angle X-ray diffraction using Ag$K\alpha$ as radiation probe. From the observed diffraction data, the total scattered intensity per atom I_a(K) was determined and Fourier transformed, to obtain the radial distribution function RDF, which revealed the closest metal-oxygen distances (r_{A-O} = 2.4Å and r_{B-O} = 2.0Å). The area under the first peak corresponds to 3.6±1 atoms, which indicates that the sum of oxygen ions about an A and a B-type ion lies between 11 and 12 atoms. The RDF of metamict samarskite appears to be typical for the short range order found in truly amorphous solids.

Introduction

Since Broegger introduced the term "metamict state" in 1890 (Faessler, 1942), there has been no convention agreed upon for how to define and characterize a mineral occurring in this metamict state. Even at the present time, the process called metamictization does not seem to be fully understood. Metamict minerals, more or less chemically complex oxides, are mostly described as being "X-ray amorphous," *i.e.*, they lack the presence of sharp diffraction peaks in an X-ray diffraction pattern. Recently, the discussion about metamictization was revived by nuclear waste technologies where crystalline and non-crystalline solids are exposed to heavy long-term irradiation (Ewing, 1981; Roy and Vance, 1981).

Two basic questions arise about the problem of the metamict state: How is it produced, and how is it defined? It is commonly agreed upon that this state originated from the crystalline form of the mineral, whereas a glass is formed from the liquid state.

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In the current literature two major hypotheses are favored by various researchers. (1) The radioactive hypothesis of formation (Holland and Gottfried, 1955; Ewing, 1975), and (2) the microcrystalline hypothesis (Bursill and McLaren, 1966; Pyatenko, 1970; Graham and Thornber, 1974). The radioactive hypothesis is based on the fact that all known metamict minerals are reported to contain U and/or Th (Bouska, 1970). Thus, their radioactive isotopes may have caused heavy radiation damage within the crystal lattice during geological periods of time. This self-irradiation leads to a disordering of the structure with a high concentration of lattice defects. As mentioned by Roy and Vance (1981), such disordering has been accomplished in the laboratory with diamond, SiO_2, $ZrSiO_4$, U_3O_8, and Al_2O_3 where the resulting structures were essentially X-ray amorphous.

In the microcrystalline hypothesis, it is assumed that the metamict minerals consist of small crystalline domains with different, but comparable structure and/or composition. Mixing and growth of the different phases is prevented by the large difference in size or charge of the oxide-forming cations.

In order to characterize a metamict mineral, most investigators (Berman, 1955; Lima de Faria, 1964;

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Komkov, 1965a; Nilssen, 1970; Ewing and Ehlmann, 1975) approached the problem in an indirect way. Heat treatment of metamict mineral systems leads to an ordering through crystallization and the formation of one or more well-defined mineral phases. Chemical compositions and crystal structures of the reaction products are compared with the composition and morphology (axial ratio) of the mineral in the metamict state in order to elucidate the crystal structure of the mineral in the pre-metamict state.

In this study, samarskite, a Nb–Ta oxide with a high content of Y, rare earth elements, and U has been investigated by the diffraction method using X-rays as the radiation probe. The purpose of this investigation was to provide data which could support one of the two hypotheses of metamictization. The large-angle diffraction, obtained with monochromatic radiation of short wavelength (Ag*K*α radiation) was subjected to a careful Fourier analysis to obtain the atomic radial distribution function of samarskite. In addition, a small-angle scattering experiment was carried out.

Diffraction theory

The scattering theory of amorphous or non-crystalline multicomponent systems has been first presented by Warren (Warren *et al.* 1936) for simple glass-forming systems like SiO_2 and B_2O_3. Recently this theory has been developed extensively for the structural characterization of metallic, semiconducting and inorganic glasses (Wagner, 1978, 1980; Wright and Leadbetter, 1976).

The intensity scattered by randomly arranged atoms of polyatomic solids or liquids can be expressed by the Debye scattering equation:

$$I_{eu}(K) = \sum_m \sum_n f_n f_m^* \sin(Kr_{mn})/Kr_{mn} \qquad (1)$$

where $I_{eu}(K)$ is the intensity of coherent scattering in electron units, $\vec{K}$ is the scattering vector of magnitude $K = 4\pi \sin\theta/\lambda$, θ is the scattering angle, λ is the wavelength of the radiation, f_m are the atomic scattering factors of atoms m (they are complex quantities when treated accurately) and $\vec{r}_{mn}$ is the difference vector of the positions of atoms m and n.

From the scattering experiment itself, the total scattered intensity per atom $I_a(K)$ can be determined by reducing the measured scattering curve adequately. In multicomponent systems $I_a(K)$ can be written as (Wagner, 1972):

$$I_a(K) = \langle f(K)^2\rangle - \langle f(K)\rangle^2 + \langle f(K)\rangle^2 I(K) \qquad (2)$$

where

$$\langle f(K)\rangle^2 = \left(\sum_i c_i f_i(K)\right)^2 \qquad (3)$$

$$\langle f(K)^2\rangle = \sum_i c_i f_i^2(K) \qquad (4)$$

$\langle f(K)\rangle$ is the average scattering factor of the sample and c_i is the concentration of element i. In this expression, any contribution of possible small angle scattering to the total scattering is neglected. $I_a(K)$ will tend towards the value of $\langle [f(K)]^2\rangle$ at large K. Therefore, the interference function I(K) defined as

$$I(K) = \{I_a(K) - [\langle f^2\rangle - \langle f\rangle^2]\}/\langle f\rangle^2, \qquad (5)$$

modulates about one at large K. This assumption proves to be quite useful when expressing the experimental intensity in electron units.

$I(K)$ is actually the sum of differently weighted quantities, called the partial interference functions $I_{ij}(K)$, which represent the correlations between atoms of type i and j. The total interference function $I(K)$ can then be written as:

$$I(K) = \sum_i \sum_j W_{ij}(K)\, I_{ij}(K) \qquad (6)$$

$W_{ij}(K)$ is the weighting factor and is defined as:

$$W_{ij}(K) = c_i c_j f_i(K) f_j(K)/\langle f(K)\rangle^2 \qquad (7)$$

This factor determines how much atomic pairs consisting of elements i and j contribute to the total scattering intensity.

It has been demonstrated that $I(K)$ can be rewritten as:

$$I(K) = 1 + \int_0^\infty 4\pi r^2[\rho(r) - \rho_0][\sin(Kr)]/(Kr)dr \qquad (8)$$

$4\pi r^2\rho(r)$ is called the radial distribution function (RDF) for the atoms and is described in such a way that $4\pi r^2\rho(r)dr$ is the number of atoms contained in a spherical shell of radius r and thickness dr surrounding the atom chosen as the origin. At large distances of r, $\rho(r)$, the actual atomic density will take the value of the average atomic density ρ_0.

Since it is the goal of the diffraction experiment to gain information about the atomic arrangement in the neighborhood of an atom chosen as the origin via the total interference function, one makes use of the fact that $I(K)$ can be expressed in terms of the RDF when Fourier transformed:

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^\infty K[I(K) - 1](\sin Kr)dK \quad (9)$$

$$G(r) = 4\pi r[\rho(r) - \rho_0]$$

$$= \frac{2}{\pi}\int_0^\infty K[I(K) - 1]\sin(Kr)dK \quad (10)$$

G(r) is called the reduced atomic distribution function, from which a "minimum" structure can be revealed.

As stated above, maxima in the RDF are related to preferred coordination shells around atoms of preference. The area under a peak is defined as the total coordination number n.

$$n = \int_{r_1}^{r_2} 4\pi r^2\rho(r)dr \quad (11)$$

For the first peak the limits r_1 and r_2 are located where the RDF is still zero and goes through the first minimum, respectively. The total coordination number n can be expressed in terms of the partial coordination number n_{ij}, which describes the number of j-type atoms around an atom of type i.

$$n_{ij} = \int_{r_1}^{r_2} 4\pi r^2\rho_{ij}(r)dr \quad (12)$$

$\rho(r)$, the atomic density and $\rho_{ij}(r)$, the number of j-type atoms per unit volume at the distance r from an i-type atom, are correlated as follows (Wagner, 1980; Wagner and Ruppersberg, 1981)

$$\rho(r) = \sum_i \sum_j c_i f_i f_j \rho_{ij}(r)/\langle f(K)\rangle^2$$

$$= \sum_i \sum_j W_{ij}(0)\rho_{ij}(r)/c_j \quad (13)$$

Thus n can be written as:

$$n = \sum_i \sum_j W_{ij}(0)n_{ij}/c_j \quad (14)$$

Unfortunately, the partial coordination numbers can be evaluated only if the partial atomic distribution functions $\rho_{ij}(r)$, the Fourier transforms of the partial interference functions $I_{ij}(r)$, are known. In general, one is limited to the total distribution function $\rho(r)$ (Equation (13)) and the total coordination number n (Equation (11)).

Experimental procedure

Samarskite is always found in a fully metamict state. For this study, a sample from Mitchell County, N.C., has been chosen. Its chemical composition has been given by Prior (1913) and Dana (1920) (Table 1), and can be approximated as: 0.06 at.% Y, 0.03 at.% U, 0.04 at.% rare earth elements, 0.12 at.% Nb, 0.04 at.% Ta, 0.06% Fe at. and 0.65 at.% O. The density was found to be 5.7 g/cm^3, and the chemical analysis was confirmed qualitatively by X-ray fluorescence spectroscopy.

It is difficult to assign a unit of structure or a crystallo-chemical formula to samarskite because it has not yet been established whether the structure of the crystalline reaction product after heat-treating is related to the original pre-metamict structure. The most common description of samarskite is that of an $A_mB_nO_x$ type oxide where the A elements include Y, U, rare earths, and Th, and the B elements include Fe, Nb, and Ta.

A small sample of samarskite was heated up in air to 1050°C for 15 minutes. X-ray powder diffraction data on the reaction product matched the data of the JCPDS-file #10-398, a samarskite investigated by Berman (1955). The reaction product could be recognized as a three-phase mixture of oxides with lattice parameters similar to $FeNbO_4$, $DyNbO_4$, and $U_3O_8 \cdot 1.5\ Nb_2O_5$ according to an earlier annealing study done by Komkov (1965a, b).

For the determination of the radial distribution function, the diffraction experiment was carried out on a bulk sample. A homogeneous slab (approximately 20 × 10 × 5 mm^3) was cut from a bulk sample, and one side was surface-ground and polished with alumina powder. This specimen was mounted in the reflection geometry on a Siemens diffractometer equipped with an evacuated sample chamber and a Si(Li) solid state detector. Ag$K\alpha$ radiation was used and electronically monochromatized with a single channel analyzer. Data were collected in a continuous θ-2θ scan, starting at 2° 2θ in intervals of 0.25° 2θ using the multichannel scaling mode of the multichannel analyzer, and ending at 90° 2θ, thus covering a range in K =

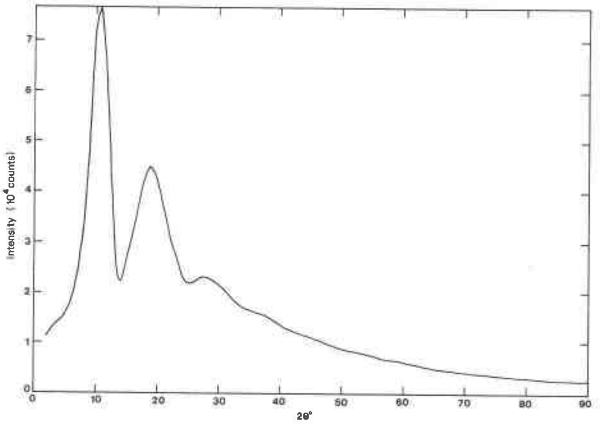

Fig. 1. X-ray diffraction pattern of a bulk samarskite sample using Ag$K\alpha$ radiation, a Si(Li) detector and the Bragg-Brentano focussing reflection geometry.

Table 1. Chemical composition and analysis of samarskite from Mitchell County, North Carolina.

	1.$^{+}$	2.$^{+,++}$	3.$^{+,++}$	4.$^{++}$
MgO	-	1.53	-	-
CaO	0.55	-	-	0.52
MnO	0.75	-	-	0.91
FeO	10.90	11.74	14.61	14.02
Y_2O_3	14.45	14.49	6.10	12.84
E_2O_3	-	-	10.80	-
CeO	-	-	-	5.17
Ce_2O_3				
La_2O_3	4.24	4.24	2.37	-
Dy_2O_3				
UO_2	-	-	-	9.91
UO_3	12.46	10.96	10.90	-
SiO_2	-	-	0.56	-
SnO_2	0.08	0.31	0.16	0.16
Nb_2O_5	37.20	55.13	41.07	54.96
Ta_2O_5	18.60	-	14.36	-
H_2O	1.12	0.72	-	0.66
density	-	5.72	5.839	5.755

$^{+}$Prior (1913) $^{++}$Dana (1920)

$4\pi\sin\theta/\lambda$ from 0.4 to 15Å^{-1}. The counting time at each interval $\Delta 2\theta = 0.25°$ was 24 min, sufficient to collect more than 3000 counts at the highest 2θ values.

A small-angle scattering experiment was performed with a Kratky camera using a powdered samarskite. It revealed no appreciable scattering at small angles due to chemical inhomogeneities and small particles or crystallites.

The measured large-angle scattering must be corrected for various factors and then normalized to absolute units, *i.e.*, the scattering per average atom with scattering factor ⟨f⟩ (Wagner, 1972). Because of the chemical composition of samarskite, only Ag$K\alpha$ radiation can be effectively used. Its wavelength is sufficiently removed from Y and Nb fluorescent radiations to permit their elimination by the solid state detector. This is not possible with Mo$K\alpha$, another short-wavelength X-ray radiation used in diffraction experiments on amorphous materials. All corrections were carried out using a RDF code on an IBM 3033 computing system (Wagner, 1967).

Results and discussion

In order to analyze the diffraction data (Fig. 1) of samarskite in terms of the scattering from an amorphous solid, some assumptions and simplifications have to be made. Since the chemical composition of samarskite is complex, nonstoichiometric and probably not homogeneous throughout the sample, only the dominant chemical elements are considered for the calculation of the interference function (Fig. 2). The chemical composition of samarskite in atomic percent used in this study reads as follows:

$$(Y_6U_3RE_4)(Nb_{12}Ta_4Fe_6)O_{65}$$

From this formula, it seems that samarskite is crystallochemically closely related to an AB_2O_6-type oxide, which is observed to have the fergusonite structure with eight O^{2-} ions about an A-type ion and four O^{2-} ions about a B-type ion (Komkov, 1959).

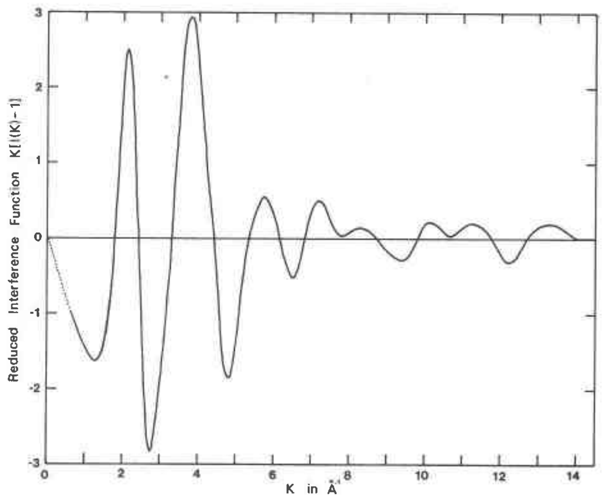

Fig. 2. Reduced total interference function K[I(K)−1] of samarskite. (I(K) is deduced from the diffraction pattern *i.e.*,

$$I(K) = \{I_a(K) - [\langle f^2\rangle - \langle f\rangle^2]\}/\langle f\rangle^2$$

where I_a(K) is the elastically scattered intensity, corrected for absorption, polarization and inelastic scattering, expressed in electron units.)

Table 2. Partial terms, weighting factors and ionic distances

Pair	$W_{ij}(0)_{AB_2O_6}$	$W_{ij}(0)_{ABO_4}$	$r_1-r_2(\text{Å})^+$	$r_{ij}(\text{Å})_{observed}$
A-A	0.107	0.139	1.98	
B-B	0.142	0.113	1.40	
C-C	0.085	0.085	2.70	
A-B	0.123	0.125	1.69	
A-C	0.111	0.103	2.34	2.4 ± 0.1
B-C	0.096	0.103	1.95	2.0 ± 0.1

$^+$average ionic radius (Cottrell, 1975)
A: Y^{3+}, U^{4+}, RE^{3+}, Fe^{2+}
B: Nb^{5+}, Ta^{5+}, Fe^{3+}
C: O^{2-}

As stated in Equation (1), the total interference function $I(K)$ is the weighted sum of the partial interference functions $I_{ij}(K)$. Because the mineral is now expressed as a quasi-ternary system, the weighting factors (Equation 2) of the partial interference functions can be calculated from the following quantities:

$$c_A = c_Y + c_U + c_{RE}$$

$$c_B = c_{Fe} + c_{Ta} + c_{Nb}$$

$$c_C = c_O$$

c_A and c_B are the sums of the individual atomic concentrations of the A and B type elements.

The assignment of the ions to the unit of structure AB_2O_6 has not been accepted generally. As discussed by Nilssen (1970) the Fe ions may appear as Fe^{2+} and Fe^{3+}. Thus, the two-valent ion should belong to the category of A ions. If we were to consider that 4.5% iron are of the Fe^{2+} variety, and the remaining 1.5% are Fe^{3+}, then we could write the crystallochemical unit of structure as ABO_4. This type of unit of structure has been proposed by Komkov (1965a) for metamict samarskite. ABO_4 type crystals are observed to have the wolframite structure with six-fold coordination of O^{2-} around the A and B type ions (Rolland and Keeling, 1957). The atomic distribution $\rho(r)$ (Equation (12)) of samarskite can be approximated by:

$$\rho(r) = W_{AA}(0)\frac{\rho_{AA}(r)}{c_A} + W_{BB}(0)\frac{\rho_{BB}(r)}{c_B} + W_{CC}(0)\frac{\rho_{CC}(r)}{c_C} + 2W_{AB}(0)\frac{\rho_{AB}(r)}{c_B} + 2W_{AC}(0)\frac{\rho_{AC}(r)}{c_C} + 2W_{BC}(0)\frac{\rho_{BC}(r)}{c_C} \quad (15)$$

A similar expression can be written for the coordination number n (Equation (13)) in terms of the partial coordination numbers n_{ij} (Equation (11)). The weighting factors $W_{ij}(0)$ of the six partial terms depend on the choice of the crystallochemical unit AB_2O_6 or ABO_4. The values of $W_{ij}(0)$ are given in Table 2 for both units of structure.

From the reduced atomic distribution function G(r) (Fig. 3), the first maximum, which contains the nearest neighbor information, appears to be broadened. It actually represents an unresolved double peak, with the main peak at r = 2.0Å and a shoulder at r = 2.4Å. These values correspond closely to the sum of the ionic radii between B and O ions and A and O ions, respectively.

We have attempted to calculate the partial coordination number from the first maximum in the RDF (Fig. 4), where information is contained about the next neighbors of both A- and B-type ions. The integral area under the peak corresponds to 3.6±0.1 atoms. A graphical separation of this peak would allow us to calculate the average number of oxygen ions around large A-type and small B-type ions, according to Equation (13). However, the partial coordination number is a very sensitive quantity and depends critically on two parameters: (1) the area under the individual peaks, *i.e.* the way we separate the double peak, and (2) the chemical composition, *i.e.*, the way we assign the various cations to the A- and B-type category. Shifting certain ions from category A to B or vice versa, influences the weighting factors $W_{ij}(0)$ for the ion

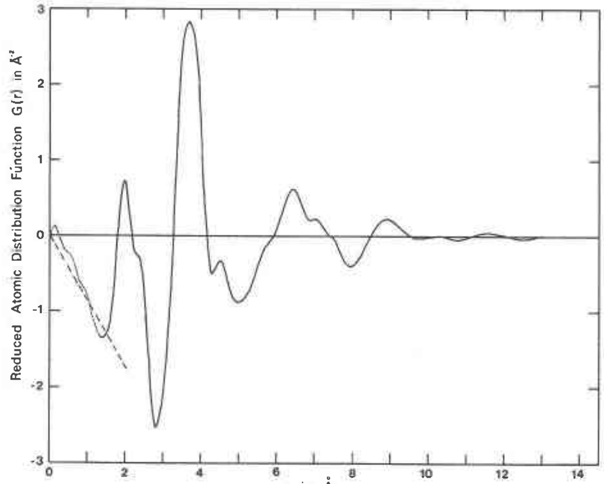

Fig. 3. Reduced atomic distribution function $G(r) = 4\pi[\rho(r)-\rho_o]$ of samarskite. (It is the Fourier transform of the reduced interference function $K[I(K)-1]$ and reveals the closest and most probable interionic distances in the sample. The negative slope of the straight dotted line yields the average atomic density $[d\ G(r)/dr]_{r\to 0} = -4\pi\rho_0$, from which the macroscopic density can be deduced).

pairs. As shown in Table 2, the weighting factors $W_{ij}(0)$ differ slightly for the units of structure AB_2O_6 and ABO_4. In the latter case, $W_{A\text{-}O}(0)$ and $W_{B\text{-}O}(0)$ are equal, but differ only by 15% for the AB_2O_6 type structure.

Assuming that the first peak is produced by the A-O and B-O ion pairs only, we can deduce the sum of the oxygen ions about the A and B type ions, *i.e.*,

$$n = 2W_{A\text{-}O}(n_{A\text{-}O}/c_O) + 2W_{B\text{-}O}(n_{B\text{-}O}/c_O)$$
$$= (2W_{A\text{-}O}/c_O)(n_{A\text{-}O} + n_{B\text{-}O})$$

From the integrated area of 3.6±0.1 atoms we calculate that the sum of oxygen ions around A and B ranges between 11 and 12 atoms. Since at this stage there is no accurate way of determining the exact area of each subpeak, we might assume that both A- and B-type ions have a six fold coordination. However, a four and eight-fold coordination as seen in fergusonite cannot be ruled out. We definitely do not believe that there will be any contribution hidden in the integrated first maximum of the RDF which results from A–A, B–B or A–B ion pairs. This is in agreement with the structure of many oxide glasses (Wright and Leadbetter, 1976).

Conclusion

In all previous diffraction studies, the potential information contained in the X-ray diffraction pattern of a fully amorphous mineral has been overlooked or ignored. Indeed the metamict state has been recognized by some researchers (Faessler, 1942; Berman, 1978) as a glassy state. But there are now attempts underway to point out the difference between the glassy and the metamict state, although the "radioactive" and "microcrystalline" hypotheses are still in question (Haaker and Ewing, 1979; Roy and Vance, 1981).

Distinguishing between microcrystalline powder structure and glassy short range order on a scale less than 20Å by diffraction is rather difficult. In a model experiment by Dixmier and Sadoc (1978), the observed interference functions and their Fourier transforms of amorphous $Ni_{80}P_{20}$ and 15 to 20Å sized Pt crystallites were compared, and it has been clearly shown that the interference functions of both systems are rather similar. But it is the RDF which characterizes the amorphous and the crystalline structure. In particular the RDF of a microcrystalline structure reveals several lattice pair distances before the local order breaks down completely and the RDF equals the average distribution $4\pi r^2\rho_0$. Similar results were found by Lu-

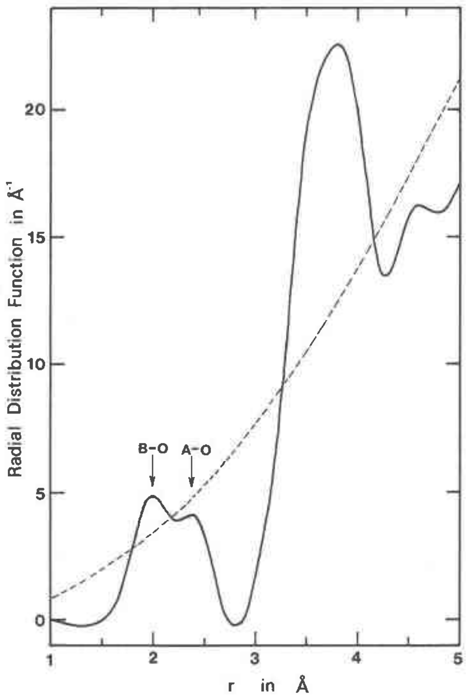

Fig. 4. Radial distribution function $RDF = 4\pi r^2\rho(r)$ (solid curve) and average atomic distribution $4\pi r^2\rho_0$ (dotted curve) of samarskite. Arrows indicate the positions of the A–O and B–O interionic distances at $r_{B\text{-}O} = 2.0$Å and $r_{A\text{-}O} = 2.4$Å.

kens and Wagner (1976) on microcrystalline Ag–Cu alloys. In the RDF of samarskite, only the first peak can be correlated to a lattice pair distance and the curve still modulates about $4\pi r^2\rho_0$ at high K. Hence samarskite can be regarded as being truly amorphous from the structural point of view. Another supporting fact for this conclusion is the true absence of small angle scattering. Microcrystalline systems should give rise to a broadening of the zero order reflection which has not been observed in the small angle experiment on samarskite powder.

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