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Crystal structure of distorted fluorite-type SrU_2O_6 with pentavalent uranium

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Abstract

Electron paramagnetic resonance absorption (EPR) of SrU_2O_6, in which the strontium and uranium atoms randomly occupy the metal sites of the fluorite-type crystal, showed a slightly anisotropic signal. In relation with this anomalous signal, the crystal structure of SrU_2O_6 has been analyzed by powder X-ray diffraction and Rietveld refinement. The sample has been found to consist of two phases with 73% and 27% in mass percent. The major phase crystallized in nearly cubic symmetry with slight rhombohedral distortion ($a=3.8642$ Å and $\alpha=60.096°$), whereas the other showed a significant rhombohedral distortion from cubic symmetry, i.e. $a=3.8334$ Å and $\alpha=62.024°$. Consequently, the existence of these two phases has been considered to be one of the possible origins which introduce the observed anisotropic signal of EPR.

Keywords: Pentavalent uranium; Electron paramagnetic resonance (EPR); Rietveld analysis; Fluorite structure; Uranium ternary compound

1. Introduction

Magnetic susceptibility and electron paramagnetic resonance (EPR) of pentavalent uranium ternary oxides with fluorite-type structure have been measured for MUO_4 (M=Sc, Y, Bi) and MU_2O_6 (M=Ca, Cd, Sr, Mg). The observed peaks at 4–7 K of magnetic susceptibility-temperature curves were analyzed by an isotropic Heisenberg model for dimers in which superexchange interaction is dominant between two uranium ions bridged through two oxygen atoms, assuming a random distribution of uranium atom and M-metal atom in the metal sites of the crystal. The EPR signals with g-factor of more than 2 were analyzed on the basis of crystal field theory i.e. pentavalent uranium with one 5f electron is in the crystal field with 8-fold cubic symmetry [1,2]. It should be noted that only SrU_2O_6 among the studied mixed oxides showed a slightly anisotropic EPR signal. So it was attempted to elucidate this anomaly.

In this work, the crystal structure of SrU_2O_6 has been studied by X-ray powder diffraction method in order to obtain a deeper understanding of the anomalous behavior of the EPR signal. The measured X-ray diffraction pattern was analyzed by Rietveld refinement starting with the space group $R\bar{3}m$.

2. Experimental

2.1. Materials

The sample of SrU_2O_6 was prepared as follows: $UO_2(CH_3COO)_2$ and $Sr(NO_3)_2$ in a molar ratio of 2:1 were dissolved in acetic acid at 353 K. The yellow powder obtained through vacuum evaporation was dehydrated by heating at 573 K for 4 h followed by heating at 1073 K in air for 40 h, giving orange colored SrU_2O_7. SrU_2O_6 was prepared by further heating as follows:

$$SrU_2O_7 \rightarrow SrU_2O_6$$

(873 K in H_2, 50 h)

SrU_2O_6 thus produced was chemically analyzed by cerium back titration method to determine the oxygen non-stoichiometry. The sample was found to be $SrU_2O_{5.51\pm0.03}$.

2.2. Measurements

2.2.1. EPR absorption spectrum

EPR spectra were recorded on a JES-RE-2X spectrometer at room temperature and liquid nitrogen temperature.

2.2.2. X-ray diffraction

X-ray diffraction analysis was carried out with a Rigaku RAD-IC diffractometer using Cu Kα radiation (40 kV, 20

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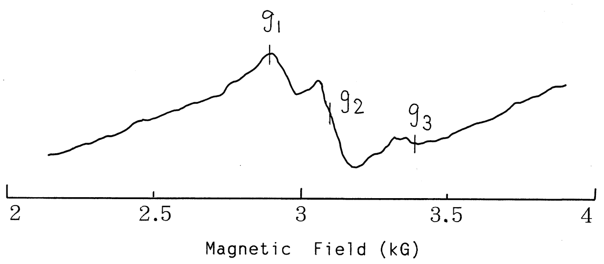

Fig. 1. EPR spectrum of distorted fluorite-type SrU_2O_6.

mA) obtained by a curved pyrolytic graphite monochromator. The slit system was 1°-1°-0.15-0.3 mm. Three measurements were made with a scanning rate 1° (2θ)/min in the 2θ range of 10–120°, during which the digital data of diffraction intensity were collected at intervals of 0.02°. The averaged intensities were used for analysis after inspection of noise intensities. The intensity and least-squares lattice parameter calculations were carried out with the LAZY-PULVERIX [3] and LCR2 [4] programs, respectively. The refinement of the crystal structure was performed by means of the Rietveld method using the RIETAN [5] program.

3. Results and discussion

An EPR signal observed for SrU_2O_6 is shown in Fig. 1. The signal is slightly anisotropic with a value of g-factor more than 2. This signal seems to originate from U^{5+} and not from U^{4+} because of EPR silence of U^{4+} in spite of having two 5f electrons. Moreover, the observed form of EPR signal reveals a superpose of an anisotropic weak signal on the isotropic strong signal of U^{5+} located in a crystal field of 8-fold cubic symmetry which was explained in detail on the basis of crystal field theory [2]. The former anisotropic signal will be discussed according to the following Rietveld refinement.

In Fig. 2, the obtained diffraction intensities of the present sample are shown as dots in the 2θ range from 10 to 120°, and the calculated result of the Rietveld refinement is given as a solid line. It is seen from the figure that the calculated line satisfactorily represents the obtained data. The ΔI value in the figure shows the difference between the observed and calculated intensities. According to the result of the refinement, the product is a mixture of the two phases, which we refer to hereafter as A and B phases, the mass percentages being 73.1 and 26.9%, respectively. Both phases crystallize in the same rhombohedral system with space group R3m, but a considerable difference was observed in the lattice parameters, i.e. $a = 3.8642$ Å and $\alpha = 60.096°$ for the A phase while $a = 3.8334$ Å and $\alpha = 62.024°$ for the B phase. If $\alpha = 60°$, the crystal reduces to a cubic system: the A phase is regarded as pseudo-cubic. In the rhombohedral cell, the uranium and strontium atoms randomly occupy the 1a(0,0,0) position with the occupancy factors 2/3 and 1/3, respectively. On the other hand, the oxygen atoms are in the $2c\pm(x,x,x)$ position with the x values close to 0.25. The U(Sr) and O atom arrangement in the crystal is similar to that in UO_2.

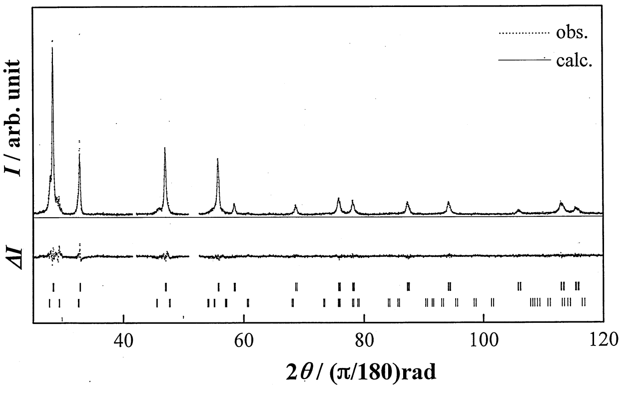

Fig. 2. Final Rietveld refinement and difference profile for $SrU_2O_{5.51\pm0.03}$.

Table 1 shows the crystal data obtained by the Rietveld refinement calculation. Although the sample was the mixture of two rhombohedral phases with the lattice parameters which were distinctly different, most reflections of the same Miller indices of these phases were partly overlapped. As a result, considerable interactions arose between the crystal parameters of the two phases leading to a stronger tendency of failure of convergence during computation. Calculation was, thus, performed by carefully selecting the initial input data as well as the computation weight. In the process, the temperature factors, which changed very sensitively and easily gave the computation error, were fixed to the reasonable values of B(Sr) = 0.5, B(U) = 0.3 and B(O) = 0.7 $Å^2$ for having rapid convergence. It is seen from Table 1 that the oxygen deficiencies in the composition of the A and B phases ($SrU_2O_{5.724}$ and $SrU_2O_{5.691}$) are consistently close to the composition by chemical analysis ($SrU_2O_{5.51\pm0.03}$), although the X-ray analysis gives slightly larger oxygen amounts. The final R_I factors obtained were 4.6 and 4.2% for A and B phases, respectively.

Table 2 shows the oxygen parameters, temperature factors and interatomic distances of the two compounds. The x value for the A phase is seen to be very close to

Table 1
Refined crystal data by the Rietveld method

	A phase	B phase
Composition	$SrU_2O_{5.724}$	$SrU_2O_{5.691}$
Mass %	73.12	26.88
a (hex, Å)	3.870(1)	3.949(2)
c (hex, Å)	9.459(2)	9.243(4)
c/a (hex)	2.444(2)	2.341(2)
a (rhomb, Å)	3.8642(5)	3.833(1)
α (rhomb, deg)	60.096(9)	62.02(2)
V (rhomb, $Å^3$)	40.89	41.63
R_I factor (%)	4.6	4.2

Table 2
Oxygen parameters, temperature factors and interatomic distances of the A and B phases

	A phase	B phase
Oxygen parameter, x	0.2500	0.2572
B (Sr, Å^2)	0.5	0.5
B (U, Å^2)	0.3	0.3
B (O, Å^2)	0.7	0.7
U(Sr)–O (Å)	2.3646	2.3774
	2.3692	2.3867
U(Sr)–U(Sr) (Å)	3.8642	3.8334
	3.8698	3.9500
O–O (Å)	2.7344	2.6799
	3.8642	2.8288
	3.8698	3.8334
		3.9500

0.25, whereas that for the B phase is significantly larger. The interatomic distances indicate that the B phase is more deformed from the cubic structure than the A phase. The larger difference in the distances is observed in the former phase.

Thus, the observed slightly anisotropic signal of EPR can be brought about by superposing the anisotropic weak signal on the isotropic strong signal. From Fig. 1, the g-values of the anisotropic signal are estimated to be about $g_1 > g_2 > g_3 \approx 2.35 > 2.19 > 1.99$, respectively, giving an average value of 2.18. This is reasonably consistent with the average g-value of 2.16 which was calculated from the wave functions obtained in the crystal field around U^{5+} with 8-fold cubic symmetry. The fact that the main cubic symmetry phase A is 73% and the rhombohedral phase B is 27% may also correspond to the signal intensity ratio of the two signals. Consequently, the existence of the two phases, one is nearly cubic symmetry phase A and the other rhombohedral phase B, has been considered to be one of the possible origins which introduce the observed anisotropic signal of EPR.

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