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EFFECTS OF IMPURITIES ON THE IRRADIATION-INDUCED LATTICE DISTORTION IN YTTRIUM NIOBATE ($YNbO_4$)

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When the $YNbO_4$ compounds containing various impurities were exposed to the fast-neutron dose, they underwent lattice-distortion to be high-temperature values in the lattice parameters; their monoclinic lattice parameters changed to smaller values in the tetragonality(a/c) in the b plane and to greater values in sinβ. The degree of the structural change increases with increasing value in the concentration of CaO subtracted by that of ZrO_2 contained.

Effects of impurities on the irradiation-induced structural changes in solids have been pointed out by several workers. Broegger[1)] suggested and Goldschmidt[2)] restated later that impurities substituting lattice sites are one of the causes for the metamictization. Adam and Cox[3)] proposed that the irradiation-induced cubic structure in ZrO_2 might be due to the impurities contained. This work was carried out to investigate impurity effects on the irradiation-induced structural changes in $YNbO_4$. It is a main component of the native fergusonite, which is usually in the metamict state[4,5)], so that the neutron irradiation of $YNbO_4$ may be a good simulation for the metamictization.

Table 1 gives the compositions of the samples irradiated. They are approximately equal to native fergusonite in composition[4,5)]. They were prepared as follows. The mixtures of oxide powder were pressed into 15ϕ×3mm pellets. They were sintered at 1400°C for 15 hr in air. The samples thus obtained were irradiated at ∼150°C in JMTR (Japan Material Testing Reactor) in a fast neutron flux (E>1MeV) of 1.5×10^{13}nv for 6 days to be 8.0×10^{18}nvt in the total flux. After the samples irradiated were cooled radioactively for several months, their lattice parameters were measured using an X-ray diffractometer. The data obtained were corrected using KCl as a standard. No significant DTA peaks due to the recovery of the radiation damage were observed up to 1000 °C for all the samples irradiated.

Table 2 gives the lattice parameters of monoclinic structure of the irradiated (irr.) and unirradiated (unirr.) samples, indicating that when irradiated the $YNbO_4$ samples decrease in the tetragonality a/c of the b plane and increase in sinβ. These structural changes due to the irradiation can be compared to the structural behavior at high temperatures. Fig. 1 gives the temperature dependence of lattice parameter in $YNbO_4$; the a/c values decrease with elevating temperature to be unity

Table 1 Composition of fergusonite-type oxides prepared. Compositions are given in mol % of substituents for Ln^{3+} sites (top) and those for Nb^{5+} sites (bottom).

	I	II	III	IV	V	VI
CaO	14.83	10.64	9.23	9.44	11.31	11.85
ZrO_2	0.97	—	—	—	7.74	1.19
1/2 Y_2O_3	84.20	89.36	90.77	90.56	80.95	86.96
MnO_2	—	—	—	0.47	—	4.00
1/2 Fe_2O_3	12.27	—	11.92	2.54	2.56	—
TiO_2	—	—	17.44	—	0.94	8.95
SnO_2	—	1.61	—	—	0.48	—
1/2 Al_2O_3	3.71	—	3.14	—	—	—
1/2 Nb_2O_5	84.02	98.39	67.50	96.99	96.02	87.05

at ∿830°C[6], where it transforms to a tetragonal structure[7]. The transition temperatures for the irradiated samples are unknown because they are too high to be measured without a recovery of the radiation damage, but the similarity between the irradiation-induced- and high-temperature structural changes strongly suggests that the structural changes due to the neutron-irradiation are attributed to lowering in the transition temperature.

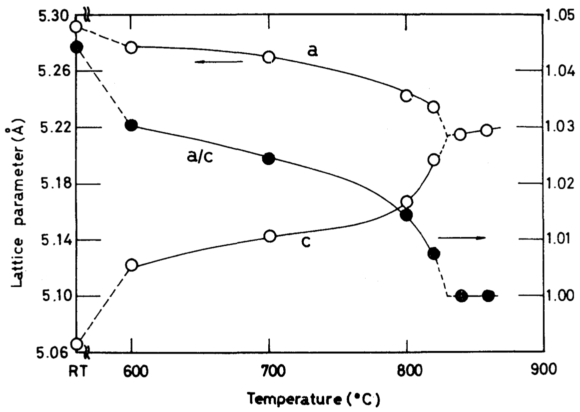

Fig. 1 Temperature dependence of lattice parameters of $YNbO_4$

The a/c change, Δ(a/c), which was calculated by subtracting $(a/c)_{irr}$ from $(a/c)_{unirr}$, was used as a standard of the structural change due to the irradiation. To see which impurity is most effective on the irradiation-induced structural change, Δ(a/c) was plotted against the impurity concentration for all the impurity components. The concentration of CaO

Table 2 Lattice parameter changes of fergusonite-type oxides due to neutron irradiation. Roman numerals refer to sample numbers shown in Table 1.

	I		II		III	
	irr.	unirr.	irr.	unirr.	irr.	unirr.
a	5.236	5.283	5.256	5.295	5.272	5.290
b	10.92	10.92	10.94	10.93	10.93	10.93
c	5.102	5.056	5.100	5.065	5.095	5.057
sinβ	0.9984	0.9971	0.9987	0.9972	0.9985	0.9971
a/c	1.0263	1.0449	1.0306	1.0454	1.0347	1.0461

	IV		V		VI		$YNbO_4$	
	irr.	unirr.	irr.	unirr.	irr.	unirr.	irr.	unirr.[9)]
a	5.264	5.288	5.269	5.289	5.248	5.290	5.285	5.292
b	10.95	10.94	10.93	10.93	10.93	10.92	10.93	10.938
c	5.102	5.065	5.081	5.062	5.079	5.055	5.072	5.066
sinβ	0.9986	0.9972	0.9981	0.9971	0.9981	0.9971	0.9971	0.9968
a/c	1.0318	1.0440	1.0370	1.0448	1.0332	1.0465	1.0420	1.0446

was found to give the most definite relationship. As shown in Fig.2, $\Delta(a/c)$ increases essentially with increasing CaO-concentration (□), but some data deviate from the straight line. Subtracting ZrO_2- from CaO-concentration improves the fitness (○); the data essentially fall on the straight line.

Thus it can be concluded that when the $YNbO_4$ compounds containing various impurities were irradiated with fast-neutron their monoclinic lattices underwent distortions to be high-temperature values in the lattice parameters and that the degree of their lattice distortions increase with increasing value in the concentration of CaO subtracted by that of ZrO_2 contained.

These impurity effects can be well understood by the feature described below. The Ca^{2+} ions substitute the Y^{3+} sites and produce 0.5 oxygen vacancies per mole of CaO-dopant[4,5)]. The Zr^{4+} ions also substitute the same sites, but produce 0.5 interstitial oxygen ions per mole of ZrO_2-dopant[4,5)]. When the CaO- and ZrO_2-dopants are added simultaneously as in this case, part of the vacant oxygen sites due to the CaO-dopant are probably filled by the excess oxygen ions due to the ZrO_2-dopant, that is, the amount of the oxygen vacancies increases with increasing value in the concentration of CaO subtracted by that of ZrO_2. The radiation defects may well be stabilized by the oxygen vacancies so that the amount of lattice defects induced by the irradiation increases with increasing concentration of the oxygen vacancies. Thus, the amount of radiation defects, or the degree of the structural changes, can be expected to increase with increasing value in the concentration of CaO subtracted by that of ZrO_2 contained.

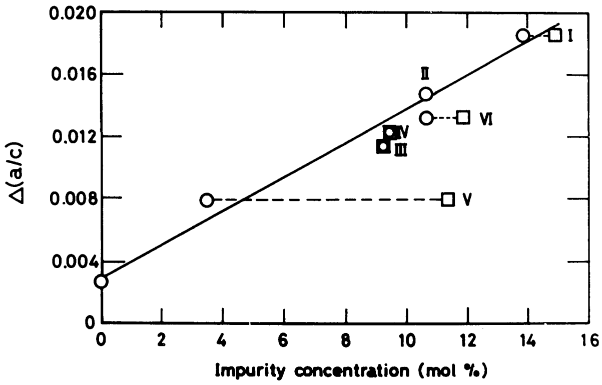

Fig. 2 Relationship between $\Delta(a/c)$ and impurity concentration (mol %).
□ : data for CaO
○ : data corrected for ZrO_2

References and Notes

1) W.C.Broegger, Salmonsens store illustrerede Konversations-lexikon 1, 742 (1893).
2) V.M.Goldschmidt, Norsk. Ak., Skr., I.1, 58 (1924).
3) J.Adams and B.Cox, Phys. Rev. Letters, 3, 543 (1959).
4) Polache, Dana's System of Mineralogy 7th Ed., V. I, p 757 New York, Wiley, 1944.
5) K.Tatsumoto, Hoshasei Kobutsu Gaisetsu, Gakugei Shuppansha, 1957.
6) H.P.Rooksby et. al.[7] obtained a value of ∿700°C as the transition temperature of $YNbO_4$. According to the data of McCarthy[8], transition temperatures of rare earth niobates elevate essentially with increasing atomic number of the rare earth elements and the transition temperatures of $DyNbO_4$ and $ErNbO_4$, which are expected to be very close to that of $YNbO_4$, are 805°C and 810°C, respectively. Therefore, the value obtained in this work is reasonable as the transition temperature of $YNbO_4$.
7) H.P.Rooksby and E.D.White, Acta. Cryst. 16, 888 (1963).
8) McCarthy, X-ray powder data file, American Society for Testing and Materials, 22-1094, 1095, 1099, 1104 and 1303.
9) Lattice parameters for the unirradiated $YNbO_4$ compound are in good agreement with the data of McCarthy[10] although small discrepancies from the data of Rooksby[7] can be seen.
10) G.J.McCarthy, Acta. Cryst. B27, 2285 (1971).

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