Radiation-induced Phase Transformations in $NdNb_{1-x}V_xO_4$

Tadao KENJO and Seishi YAJIMA

The Oarai Branch, The Research Institute for Iron, Steel and Other Metals, Tohoku University, Oarai-machi, Ibaraki 311-13

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When $NdNb_{1-x}V_xO_4$ compounds were exposed to a fast neutron dose of 6.6×10^{18} *nvt*, their monoclinic-tetragonal transition temperatures were lowered; particularly the transition temperature for the compound with $x=0.3$ was lowered to a temperature below room temperature. The lowering of the transition temperatures was greater for samples containing more V^{5+} ions. Although the present work does not fully reveal why neutron-irradiation lowers the transition temperature, it does show that neither the internal stress due to radiation damage nor the change in valency state of Nb^{5+} or Nd^{3+} lowers the transition temperature.

In previous work it was found that when the $YNbO_4$ compounds containing various impurities were exposed to a fast-neutron dose, the monoclinic $YNbO_4$ lattice approached a tetragonal structure; the a/c ratio of the monoclinic lattice became closer to unity.[1] This radiation-induced structural change can be explained as being due to (1) the presence of the high-temperature phase (tetragonal form) which is formed by quenching by the thermal spike mechanism, or (2) a lowering of the transition temperature (T_t), as will be described in more detail in a later section. One can expect no changes in T_t from (1), while a lowering of T_t can be expected from (2). Therefore, a measurement of T_t for the irradiated samples would determine which explanation is valid. In previous work, however, the T_t of the irradiated samples could not be measured without recovery of the damage due to radiation because this process begins at a temperature below T_t. This work employed the doping method in order to lower T_t to a temperature below the recovery temperature. Vanadium oxide (V_2O_5) was chosen as a dopant which may lower the T_t of $LnNbO_4$ (Ln=a rare earth) for the reasons described below. (1) Vanadium belongs to the same family of the periodic table as niobium and thus their chemical properties are similar so that the substitution of Nb^{5+} by V^{5+} can be expected to be efficient. (2) The ABO_4 scheelite-type oxides appear to form a tetragonal structure when the ionic potential (Z/r, Z=ionic charge, r=ionic radius) of ions at the A site is small and that at the B site is great, *e.g.*, for $CaWO_4$, $BaMoO_4$ and $NaIO_4$,[2] while they appear to be distorted to a monoclinic structure in the opposite case, *e.g.*, for $LnNbO_4$ and $LnTaO_4$.[2,3] The V^{5+} dopant (Z/r of $Nb^{5+}=7.25$, Z/r of $V^{5+}=8.47$) enhances the mean ionic potential of the Nb^{5+} sites so that, for the above-mentioned reason, V^{5+} can be expected to stabilize the tetragonal structure of $LnNbO_4$ in such a way that the more V^{5+} ions that the $LnNbO_4$ samples contain, the greater will be the T_t lowering.

Neodymium was used as Ln because the T_t of $NdNbO_4$ is one of the lowest of the $LnNbO_4$ family[4] and because it is induced to only a weak radioactivity upon reactor irradiation.

Experimental

Samples were prepared by the usual ceramic technique, as described previously.[1] The oxide mixtures were milled in a mortar and pressed into $15\phi\times3$ mm pellets, which were then heated to 1400 °C in air for 15 h. The samples thus obtained were irradiated in the JMTR (Japan Material Testing Reactor) at a temperature of 150 °C by a fast-neutron flux ($E>1$ MeV) of 1.9×10^{13} *nv* for 4 days, for a total flux of 6.6×10^{18} *nvt*.

The lattice parameters of the irradiated and non-irradiated samples were calculated using the data obtained from X-ray powder patterns using KCl as an internal standard. Since no DTA peaks for the phase transformation were observed, a high-temperature X-ray diffractometer was used for the measurements of T_t.

The magnetic susceptibility was measured using a Gouy balance.

Results and Discussion

The crystal structure of V_2O_5-doped $NdNbO_4$ compounds was identified as a monoclinic-distorted scheelite structure; the X-ray diffraction powder patterns could be indexed according to the known data for monoclinic

TABLE 1. LATTICE PARAMETER CHANGES DUE TO NEUTRON IRRADIATION OF $NdNb_{1-x}V_xO_4$ (v=unit cell volume)

x	irr./ nonirr.	Temp	a(Å)	b(Å)	c(Å)	sinβ	a/c	v(Å^3)
0.1	nonirr.	R.T.	5.441	11.333	5.157	0.9979	1.0551	317.29
	irr.	R.T.	5.431	11.331	5.169	0.9982	1.0507	317.49
0.2	nonirr.	R.T.	5.391	11.377	5.172	0.9988	1.0423	316.83
	irr.	R.T.	5.378	11.383	5.195	0.9991	1.0352	317.74
0.3	nonirr.	R.T.	5.346	11.416	5.193	0.9994	1.0295	316.73
	irr.	R.T.	5.276	11.423	5.276	1	1	317.97
	irr.	liq. N_2	5.354	11.383	5.181	0.9995	1.0335	315.55
	irr.	0 °C	5.31	11.42	5.25	0.9999	1.010	318

$LnNbO_4$ structures.[4] Table 1 gives the lattice parameters for the irradiated (irr.) and non-irradiated (nonirr.) $NdNb_{1-x}V_xO_4$ samples. Since the dependence of the lattice parameters of the non-irradiated samples on the V_2O_5 concentration is smooth, the V_2O_5-doped $NdNbO_4$ samples can be regarded as solid solutions. The reduction in the unit cell volume with increasing V_2O_5 content is reasonable because V^{5+} is smaller than Nb^{5+}.

Table 1 indicates that the $NdNb_{1-x}V_xO_4$ compounds approach tetragonal structures (the compound with $x=0.3$ becomes tetragonal) when they are irradiated; a/c and $\sin\beta$ become closer to unity (these parameters become unity for $x=0.3$) with increasing irradiation. These lattice parameter changes due to irradiation can be explained as being due to (1) the presence of the high-temperature phase formed by the thermal spike mechanism, or (2) a lowering of T_t, as mentioned above. The problem to be solved is to determine which explanation is valid.

In the thermal spike process, small regions of the solid are heated for a very short time and followed by very rapid cooling. If the heating process raises the local temperature high enough for transformation to a high-temperature form, the thermal-spiked areas maintain the high-temperature structure, at least when the local temperature is higher than T_t. The high-temperature phase thus formed is quenched as a metastable phase if the cooling rate of the thermal-spiked regions is so high that the high-temperature structure formed cannot return to the low-temperature structure. Due to this thermal spike process the samples irradiated thus consist of a quenching-formed high-temperature phase and an unchanged low-temperature phase and the fractional portion of the former phase present increases with increasing irradiation dose. The thermal-spiked region is expected to be a sphere of approximately a few tens of Å in diameter and the X-ray diffraction patterns for the high-temperature phase thus formed cannot be separated from those for the low-temperature phase, that is, the lattice parameters in this case denote mean values of the above two phases. The presence of the tetragonal structure thus formed renders the mean values of a/c and $\sin\beta$ closer to unity. This is observed in the case of $x=0.1$ and 0.2 (Table 1). When the whole region of the solid has been covered with rapidly-quenched high-temperature phase islands, the radiation-induced phase transformation is completed. This is the case for $x=0.3$. Thus, as far as the lattice parameters at room temperature are concerned, the thermal spike mechanism explains the radiation-induced structural changes in $NdNb_{1-x}V_xO_4$.

The radiation-induced structural changes can also be explained as being due to a lowering of T_t. The values of a/c and $\sin\beta$ for $LnNbO_4$ approach unity with increasing temperature and become unity at T_t, where the $LnNbO_4$ transforms from monoclinic to tetragonal form.[1,3] Therefore, if the T_t of $NdNb_{1-x}V_xO_4$ is lowered due to the irradiation, the a/c and $\sin\beta$ values at room temperature become closer to unity. This is the case for $x=0.1$ and 0.2. If T_t is lowered due to the irradiation to a temperature below room temperature, the crystal structure at room temperature is tetragonal. This is the case for $x=0.3$.

If the lattice parameter changes due to irradiation are ascribable to the fractional portion of the tetragonal phase formed by process (1), the transition temperature is unchanged upon irradiation because the process (1) does not change the T_t for the monoclinic phase and because the tetragonal phase formed by the rapidly-quenching process does not contribute to the T_t shift. On the other hand, if the lattice parameter changes are due to a lowering of T_t, the transition temperature is lowered by the irradiation. Therefore, measuring the T_t of the irradiated samples determines which explanation is valid.

The irradiated $NdNb_{0.7}V_{0.3}O_4$ sample has a tetragonal structure. If the tetragonal structure is ascribed to the thermal spike process, then when the irradiated $NdNb_{0.7}V_{0.3}O_4$ sample is cooled it maintains its tetragonal structure at any temperature below room temperature. On the other hand, if this structure is the result of the lowering of T_t to a temperature below room temperature, the tetragonal form is transformed into a monoclinic structure when the irradiated sample is cooled to a temperature that is lower than T_t but still high enough for the transformation rate. As is shown in the last line of Table 1, the values of $\sin\beta$ and a/c at 0 °C show small deviations from unity, or a slight distortion to the monoclinic form. The values at liquid N_2 temperature (the next to the last line in the same table) show greater deviations from unity. These findings indicate that the tetragonal structure in the irradiated $NdNb_{0.7}V_{0.3}O_4$ sample is due to a lowering of T_t to a temperature below room temperature, that is, explanation (2) is valid.

Figure 1 gives the temperature dependence of the lattice parameters for both irradiated (○) and non-irradiated (●) $NdNb_{0.8}V_{0.2}O_4$. From the figure, the T_t for the irradiated sample is found to be ≈290 °C and that the non-irradiated sample to be ≈330 °C.

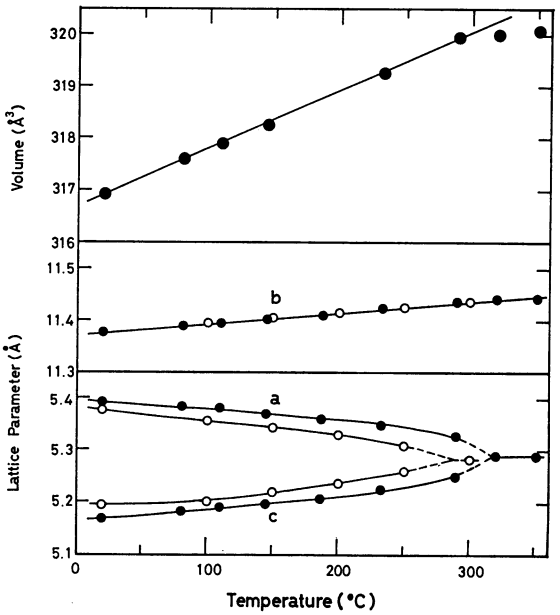

Fig. 1. Temperature dependence of lattice parameters of $NdNb_{0.8}V_{0.2}O_4$.
●: Non-irradiated, ○: irradiated.

TABLE 2. TRANSITION TEMPERATURES (T_t) FOR IRRADIATED AND NON-IRRADIATED $NdNb_{1-x}V_xO_4$

x	irr./nonirr.	T_t(°C)
0.1	nonirr.	520
	irr.	≈510
0.2	nonirr.	330
	irr.	290
0.3	nonirr.	170
	irr.	20

This indicates that the radiation-induced lattice distortion in $NdNb_{0.8}V_{0.2}O_4$ is also due to a lowering of T_t. Similarly, the high-temperature X-ray diffraction data indicate that the T_t of the $NdNb_{0.9}V_{0.1}O_4$ sample is also lowered upon irradiation, although the data are not given. Table 2 summarized the results of T_t for the irradiated and non-irradiated $NdNb_{1-x}V_xO_4$ samples, indicating that their transition temperatures are lowered when they are irradiated. Thus, it has been shown that the radiation-induced structural changes in $NdNb_{1-x}V_xO_4$ are due to a lowering of T_t, and not due to the rapidly-quenched tetragonal phase. Table 2 also indicates that the T_t lowering due to irradiation is greater in samples containing more V_2O_5 dopant. Although this cannot be explained at present, we suppose that the lattice distortion induced by the dopant plays a role in stabilizing the radiation damage.

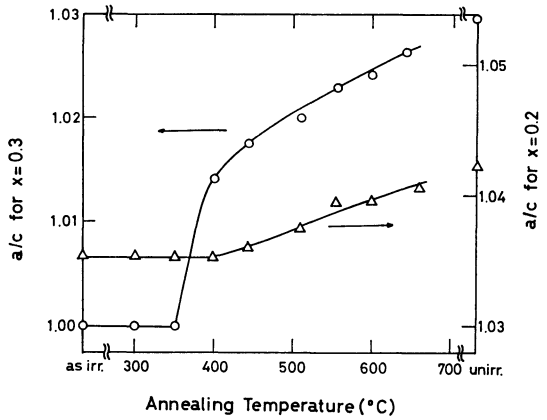

Fig. 2. Variation of a/c with annealing temperature in $NdNb_{0.8}V_{0.2}O_4$ (△) and $NdNb_{0.7}V_{0.3}O_4$ (○) irradiated.

To confirm that the sample does not recover from radiation damage while T_t is being measured, a study of the annealing of the irradiated samples was carried out. The samples were annealed successively at each temperature for 1 h in air. Figure 2 shows the variation of a/c for the irradiated $NdNb_{0.8}V_{0.2}O_4$ and $NdNb_{0.7}V_{0.3}O_4$ samples with the annealing temperature, indicating that the radiation damage recovery begins at ≈350 °C. Neither of the values of T_t for the two samples is higher than that. The data for the annealing of $NdNb_{0.9}V_{0.1}O_4$ could not be obtained because the a/c change due to irradiation is too small. However, the amount of damage recovery during the T_t measurements, if any, could be considered to be very small due to the fact that the lattice parameters of the irradiated sample are essentially the same before heating as those of the same sample after heating to 520 °C (520 °C= the T_t of $NdNb_{0.9}V_{0.1}O_4$). Thus, it has been shown that the T_t values for the irradiated samples involve no recovery effects of the radiation damage.

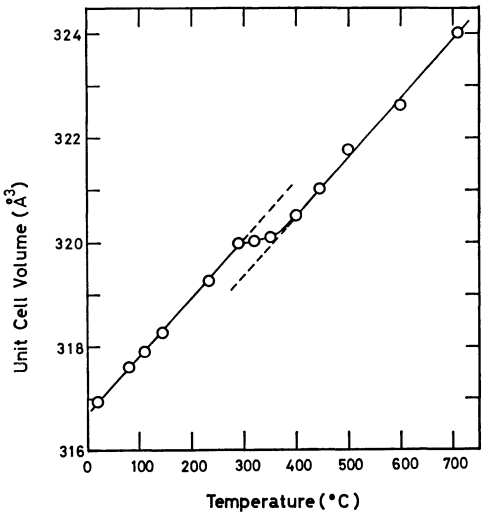

Fig. 3. Temperature dependence of unit cell volume of $NdNb_{0.8}V_{0.2}O_4$.

Several materials undergo similar shifts in transition temperatures when exposed to fast-neutron doses.[5-9,11-13] However, it is not yet clearly understood why their transition temperatures vary due to irradiation. Some workers have attributed this to the internal stress caused by radiation damage; the internal stress acts on T_t as if a pressure had been applied. However, this explanation may not be valid for the reason described below. As is shown in Fig. 3, the unit cell of $NdNb_{0.8}V_{0.2}O_4$, which is an example of $NdNb_{1-x}V_xO_4$, shrinks when it transforms from a monoclinic to a tetragonal structure. Therefore, if such an internal stress lowers T_t, it must act as a positive pressure on T_t, as predicted by the Clausius-Clapeyron equation. When a positive pressure is applied the crystal lattice shrinks. Therefore, such radiation-induced internal stress shrinks the unit cell, that is, the irradiation must result in the shrinking the unit cell. However, on the contrary, the unit cells of $NdNb_{1-x}V_xO_4$ expand when they are irradiated (Table 1). This contradiction strongly suggests that the internal stress due to the radiation damage, if at present at all, is not the dominant cause of the T_t lowering.

The experimental results of the neutron-irradiation of $BaTiO_3$[9] also appear to disprove the "internal stress theory." The $BaTiO_3$ compound is transformed from a tetragonal to a cubic structure at 130 °C. It undergoes T_t lowering when it is irradiated.[9] In a manner similar to the case of $NdNb_{1-x}V_xO_4$, a positive pressure must be assumed[10] as the internal stress to explain the T_t lowering due to the irradiation. However, in reality, the unit cell expands upon irradiation.[9] This contradicts the assumption that the internal stress acts as a positive pressure.

The radiation-induced lowering of T_t may be explained as being due to a change in the valency state. As described in the previous section, the $NdNbO_4$ compound appears to suffer a lowered T_t when replacing the Nb^{5+} ion with ions of greater ionic potential or

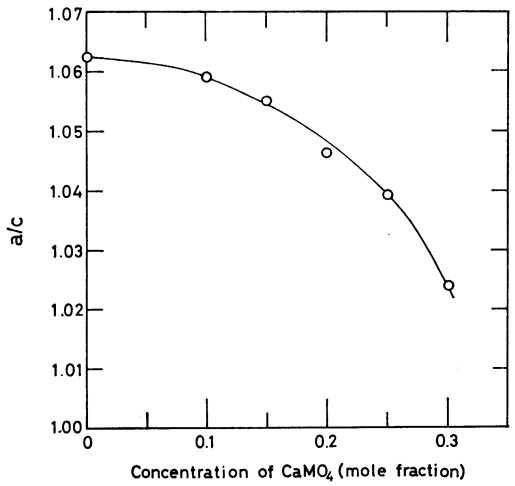

Fig. 4. Variation of a/c with concentration of $CaMoO_4$ in $NdNbO_4$.

when replacing the Nd^{3+} ions with ions of lower ionic potential. In fact, as shown in Fig. 4, the $CaMoO_4$ dopant for which the ionic potential of Ca^{2+} ($Z/r=2.02$) is smaller than that of Nd^{3+}($Z/r=2.88$) and that of Mo^{6+}($Z/r=9.68$) is greater than that of Nb^{5+}($Z/r=7.25$), lowers the a/c ratio of $NdNbO_4$, that is, it lowers the T_t of $NdNbO_4$. A similar effect on T_t occurs for a change in valency state. If electrons are transferred from Nb^{5+} to Nd^{3+} and are trapped there when the $NdNbO_4$ compound is irradiated, the irradiated $NdNbO_4$ compound contains $Nd^{2+}Nb^{6+}O_4$. It can be expected that the ionic potential of Nd^{2+} is smaller than that of Nd^{3+} and that the ionic potential of Nb^{6+} is greater than that of Nb^{5+}. Therefore, if irradiation induces the $Nd^{2+}Nb^{6+}O_4$ compound in the $NdNbO_4$ matrix, the effect on the T_t of $NdNbO_4$ may well be similar to that of the $CaMoO_4$-dopant, that is, the $Nd^{2+}Nb^{6+}O_4$ compound will lower the T_t of $NdNbO_4$.

The $Nd^{2+}Nb^{6+}O_4$ compound may be detected by measuring the magnetic susceptibility of the sample It is reasonable to expect that Nd^{2+} shares 4 Bohr magnetons/mol and Nb^{6+} 1 Bohr magneton/mol while the non-irradiated $NdNbO_4$ compound retains 3 Bohr magnetons/mol.[14] V^{5+} is diamagnetic. Therefore, if $Nd^{2+}Nb^{6+}O_4$ is present in the irradiated sample, the magnetic susceptibility of the irradiated sample will be greater than that of non-irradiated sample by 2 Bohr magnetons per mol due to the $Nd^{2+}Nb^{6+}O_4$ present. The $CaMoO_4$ doping data (Fig. 4) leads to the estimation that, if the radiation-induced $Nd^{2+}Nb^{6+}O_4$ compound lowers the T_t of a $NdNb_{0.7}V_{0.3}O_4$ sample, at least one tenth mole of $Nd^{2+}Nb^{6+}O_4$ must be present in the irradiated $NdNb_{0.7}V_{0.3}O_4$ samples. Such an amount of $Nd^{2+}Nb^{6+}O_4$ can readily be detected using a Gouy balance. Figure 5 gives the temperature dependence of the magnetic susceptibilities of irradiated (○) and non-irradiated (△) $NdNb_{0.7}V_{0.3}O_4$. However, no significant difference in the magnetic susceptibilities between the two is observed. Therefore, the change in the valency state is not an important cause of the radiation-induced lowering of T_t.

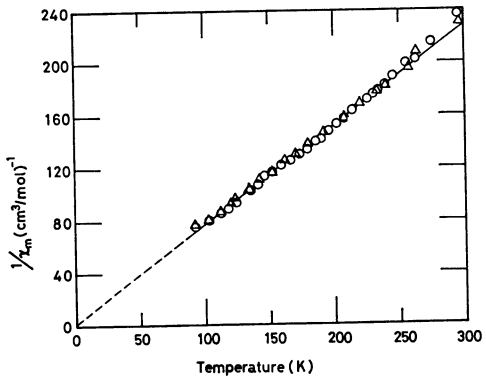

Fig. 5. Temperature dependence of inverse molar susceptibility in irradiated (○) and non-irradiated (△) $NdNb_{0.7}V_{0.3}O_4$ sample.

This study provides no definite explanation of the radiation-induced lowering of T_t, but it is supposed that this may be ascribed to disordering in the crystal lattice.

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