JOURNAL OF SOLID STATE CHEMISTRY 95, 438–442 (1991)

BRIEF COMMUNICATIONS

Synthesis and Magnetic Property of $NaFe_3V_9O_{19}$

Y. KANKE,* E. TAKAYAMA-MUROMACHI, Y. UCHIDA, K. KATO,
AND S. TAKEKAWA

*National Institute for Research in Inorganic Materials, 1-1 Namiki,
Tsukuba, Ibaraki 305, Japan*

Received June 17, 1991

A new phase, $NaFe_3V_9O_{19}$, was found. It crystallizes hexagonal with $a = 5.8400 \pm 0.0001$ and $c = 22.8058 \pm 0.0005$ Å. Its possible space groups are $P6_3/mmc$, $P\bar{6}2c$, or $P6_3mc$. The composition and the crystal data indicate that $NaFe_3V_9O_{19}$ is isostructural with magnetoplumbite-type compounds. $NaFe_3V_9O_{19}$ shows a uniaxial magnetism with the easy axis of magnetization parallel to [001] below the transition temperature, around 240 K. © 1991 Academic Press, Inc.

Introduction

Both $BaFe_{12}O_{19}$ and $LaFe_{12}O_{19}$ take magnetoplumbite-type crystal structures (hexagonal, $P6_3/mmc$) (*1*) and show uniaxial ferrimagnetisms (*2–7*) with the easy axes of magnetization parallel to [001], below the Néel temperatures of 723 K (*8*) and 695 K (*9*), respectively. Their resistivity at room temperature is 10^8 Ω cm for $BaFe_{12}O_{19}$ and 10^1 Ω cm for $LaFe_{12}O_{19}$ (*10*). Their magnetic structures have been described based on the localized *d*-electron models (*2–7*), though $LaFe_{12}O_{19}$ has rather low resistivity and contains mixed-valent iron ions.

NaV_6O_{11} was first synthesized by de Roy *et al.* (*11*) and revealed to be structurally related to magnetoplumbite (*12*). NaV_6O_{11} crystallizes in $P6_3/mmc$ (*12*), shows a magnetic phase transition at 64.2 K (*13, 14*), and exhibits uniaxial magnetic anisotropy with the easy axis of magnetization parallel to [001] below the transition temperature (*14*). The spontaneous magnetization of NaV_6O_{11} at 5 K is 1.7 μ_B per formula unit (*14*). The resistivity of NaV_6O_{11} perpendicular to [001] shows an anomaly at the transition temperature (*13, 14*) as in the case with the resistivity of ferromagnetic metals, while that parallel to [001] does not show such an anomaly (*14*). We indicated that itinerant *d*-electrons play some important roles in magnetism of NaV_6O_{11} (*14*), in contrast to $BaFe_{12}O_{19}$ and $LaFe_{12}O_{19}$ (*2–7*).

SrV_6O_{11} and $SrT_xV_{6-x}O_{11}$ (T = Ti, Cr, and Fe) were found and confirmed to be isostructural with NaV_6O_{11} (*12, 15*). The T ions do not localize at a particular site in $SrT_xV_{6-x}O_{11}$ phases (*15*).

In the present study, a new magnetoplumbite-type phase, $NaFe_3V_9O_{19}$, was found. Its magnetic property and electrical resistivity were studied using sintered samples. Though a number of magnetoplumbite-type phases ($AB_{12}O_{19}$) have so far been investigated, the formal charge of A ion has

---

* To whom correspondence should be addressed.

0022-4596/91 $3.00

TABLE I

X-RAY POWDER PATTERN OF $NaFe_3V_9O_{19}$

h	k	l	d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l	d_{obs}/Å	d_{calc}/Å	I/I_0	h	k	l	d_{obs}/Å	d_{calc}/Å	I/I_0
0	0	2	11.358	11.403	60	0	0	14	1.6291	1.6290	22	3	2	5	1.1244	1.1245	<1
0	0	4	5.689	5.701	41	3	0	4	1.6167	1.6167	10	1	0	20	1.1123	1.1124	2
1	0	0	5.056	5.058	4	2	0	11	1.6032	1.6033	50	2	1	17	1.0981	1.0981	2
1	0	1	4.933	4.938	6	2	1	8	1.5875	1.5877	9	3	2	7	1.0931	1.0930	2
1	0	3	4.207	4.211	20	3	0	6	1.5412	1.5411	2	2	2	14	1.0872	1.0872	3
0	0	6	3.797	3.801	15	2	0	12	1.5192	1.5193	11	4	1	4	1.0836	1.0835	3
1	0	5	3.385	3.387	14	2	2	0	1.4599	1.4600	19	4	0	11	1.0795	1.0795	4
1	0	6	3.0373	3.0385	11	2	0	13	1.4415	1.4414	7	3	2	8	1.0746	1.0747	1
1	1	0	2.9192	2.9200	20	0	0	16	1.4253	1.4254	2	1	1	20	1.0621	1.0622	1
0	0	8	2.8495	2.8507	43	2	1	11	1.4056	1.4054	1	4	1	6	1.0598	1.0599	1
1	0	7	2.7380	2.7389	100	3	1	3	1.3795	1.3794	1	2	1	18	1.0562	1.0561	2
1	1	4	2.5980	2.5990	67	1	0	16	1.3722	1.3719	4	4	0	12	1.0526	1.0527	1
2	0	0	2.5293	2.5288	4	2	0	14	1.3693	1.3694	10	0	0	22	1.0367	1.0366	4
2	0	1	2.5127	2.5134	14	3	1	4	1.3622	1.3621	1	4	0	13	1.0258	1.0257	1
1	0	8	2.4832	2.4834	30	2	1	12	1.3479	1.3478	3	2	1	19	1.0167	1.0165	1
2	0	2	2.4671	2.4688	5	3	1	5	1.3403	1.3407	<1	3	0	18	1.0129	1.0128	3
2	0	3	2.3992	2.3995	17	2	0	15	1.3030	1.3030	1	5	0	1	1.0106	1.0105	<1
1	1	6	2.3153	2.3156	13	2	2	8	1.2996	1.2995	3	5	0	2	1.0077	1.0076	<1
0	0	10	2.2812	2.2806	1	1	0	17	1.2964	1.2967	5	4	0	14	0.9986	0.9988	1
2	0	5	2.2110	2.2116	17	2	1	13	1.2926	1.2925	1	3	2	12	0.9904	0.9903	<1
2	0	6	2.1049	2.1054	16	3	1	7	1.2883	1.2884	4	2	1	20	0.9794	0.9793	1
1	1	8	2.0399	2.0398	1	1	1	16	1.2811	1.2809	1	1	0	23	0.9729	0.9730	<1
2	0	7	1.9980	1.9976	4	0	0	18	1.2672	1.2670	1	3	1	17	0.9695	0.9695	1
1	0	11	1.9184	1.9183	2	3	1	8	1.2589	1.2586	2	5	0	7	0.9659	0.9660	1
0	0	12	1.9006	1.9005	1	2	0	16	1.2414	1.2417	1	4	2	1	0.9549	0.9550	1
2	0	8	1.8917	1.8917	2	1	0	18	1.2292	1.2290	6	5	0	8	0.9532	0.9533	1
2	1	3	1.8531	1.8539	1	4	0	5	1.2185	1.2184	<1	0	0	24	0.9502	0.9502	1
2	0	9	1.7897	1.7900	2	4	0	6	1.1998	1.2000	1	4	2	3	0.9483	0.9483	1
1	0	12	1.7785	1.7790	11	2	0	17	1.1852	1.1851	1	3	3	6	0.9428	0.9429	<1
2	1	5	1.7629	1.7630	2	4	0	7	1.1790	1.1787	<1	3	1	18	0.9403	0.9402	1
2	1	6	1.7079	1.7078	2	1	0	19	1.1677	1.1679	3	1	0	24	0.9338	0.9339	1
2	0	10	1.6935	1.6936	8	1	1	18	1.1623	1.1623	7	4	2	6	0.9269	0.9269	<1
3	0	0	1.6853	1.6859	3	3	2	3	1.1471	1.1470	<1	2	0	23	0.9231	0.9231	1
1	0	13	1.6568	1.6574	1	0	0	20	1.1403	1.1403	5	3	1	19	0.9120	0.9120	1
2	1	7	1.6487	1.6487	18	3	1	12	1.1285	1.1286	1	1	1	24	0.9036	0.9036	<1
												2	2	20	0.8987	0.8987	2

been restricted to between +2 and +3. To the best of our knowledge, the main cation for B has been restricted to Al^{3+}, Fe^{3+}, and Ga^{3+}.

Experimental

V_2O_4 was prepared by heating an equimolar mixture of V_2O_5 (99.9%) and V_2O_3 in a sealed silica tube at 1273 K for 3 days. The V_2O_3 had been obtained by reducing the V_2O_5 in hydrogen at 1073 K. β-$NaFeO_2$ was prepared by heating an equimolar mixture of Na_2CO_3 (99.9%) and Fe_2O_3 (99.9%) at 1073 K for 1 day with an intermediate grinding.

β-$NaFeO_2$, Fe_2O_3, V_2O_4, and V_2O_3 were mixed in a 1 : 1 : 0.5 : 4 molar ratio. About 3.0 g of the mixture were placed in a platinum capsule, sealed in an evacuated silica tube,

TABLE II

LATTICE PARAMETERS OF $NaFe_3V_9O_{19}$ AND RELATED COMPOUNDS

Compound	a/Å	c/Å
$NaFe_3V_9O_{19}$	5.8400(1)	22.8058(5)
$SrFe_{12}O_{19}$[a]	5.8868(5)	23.037(2)
$BaFe_{12}O_{19}$[b]	5.893	23.194
$LaFe_{12}O_{19}$[c]	5.879	22.8807
$CaAl_{12}O_{19}$[d]	5.5579(6)	21.905(20)
$SrAl_{12}O_{19}$[e]	5.585	22.07
$SrGa_{12}O_{19}$[f]	5.796	22.84

[a] From Ref. (*16*).
[b] From Ref. (*1*).
[c] From Ref. (*10*).
[d] From Ref. (*17*).
[e] From Ref. (*18*).
[f] From Ref. (*19*).

and then heated at 993 K for 1 day. After it was cooled to room temperature, the product was ground and identified by X-ray powder diffraction with Cu*Kα* radiation. This procedure was repeated until its X-ray powder pattern changed no longer. Three heating runs (1 + 3 + 3 days) were required to obtain pure $NaFe_3V_9O_{19}$. The formation of the phase became sluggish at 973 K and it required two weeks of heating period to obtain a pure sample. The phase decomposed above 1073 K. To prepare the specimens for the magnetization and resistivity measurements, powdered $NaFe_3V_9O_{19}$ was pressed into a pellet and heated at 993 K in the same way as mentioned above. EPMA measurement was carried out using NaV_6O_{11} and $YFeO_3$ as standard materials.

The magnetization of $NaFe_3V_9O_{19}$ was measured by a SQUID magnetometer using 6.84 mg of the above-mentioned sintered sample. The resistivity of $NaFe_3V_9O_{19}$ was measured by the standard four-probe method.

Results and Discussion

The X-ray powder diffraction pattern of $NaFe_3V_9O_{19}$ is shown in Table I. All of the reflections can be indexed applying a hexagonal crystal system and space group $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$. EPMA measurement showed its composition to be Na : Fe : V = 1 : 2.8(2) : 9.0(4), which confirms that the phase belongs to the magnetoplumbite. A detailed Rietveld analysis of the neutron powder diffraction data is now in progress. Preliminary refinement also supported the magnetoplumbite-type structure for $NaFe_3V_9O_{19}$. The compositional range of x for $NaFe_xV_{12-x}O_{19}$ was examined by the X-ray powder diffraction of the samples with x = 2.8, 3.0, and 3.2. The sample with x = 2.8 was single-phased, however, there were no detectable shifts between the diffraction data of "$NaFe_{2.8}V_{9.2}O_{19}$" and those of $NaFe_3V_9O_{19}$. The sample with x = 3.2 contained a corundum-type phase, however, there were slight but obvious shifts between the diffraction data of $NaFe_3V_9O_{19}$ and those of "$NaFe_{3.2}V_{8.8}O_{19}$." At the present stage, we can not conclude whether or not there is a homogeneity range of x for $NaFe_xV_{12-x}O_{19}$. The lattice parameters of $NaFe_3V_9O_{19}$ are listed in Table II, together with those of known magnetoplumbite-type phases.

Typical grains of $NaFe_3V_9O_{19}$ as obtained

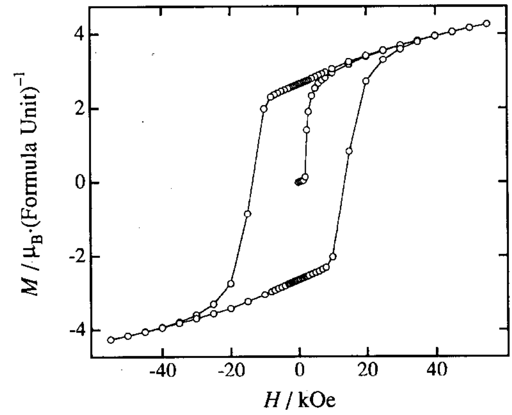

FIG. 1. Magnetization vs. external magnetic field of a sintered $NaFe_3V_9O_{19}$ sample at 5 K.

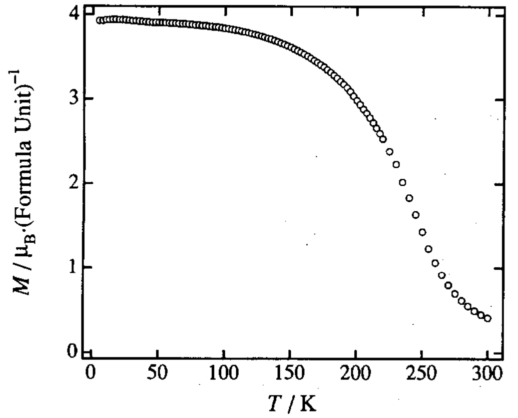

FIG. 2. Magnetization vs. temperature of a sintered $NaFe_3V_9O_{19}$ sample at 4 T.

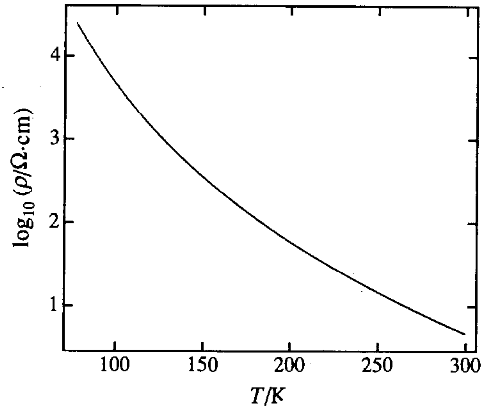

FIG. 3. Logarithmic resistivity vs. temperature of a sintered $NaFe_3V_9O_{19}$ sample.

were thin hexagonal plates of ca. 10 μm in diameter. A microscopic observation at low temperatures showed that the grains were attracted by a magnet and their [001] directions were oriented parallel to the lines of magnetic force. Figure 1 shows the magnetization of a sintered $NaFe_3V_9O_{19}$ sample vs. external magnetic field at 5 K. The data resulted in a hysteresis loop and the coercive force was ca. 14 kOe. Figure 2 shows the temperature dependence of the magnetization in an external magnetic field of 4 T. The above results show that $NaFe_3V_9O_{19}$ exhibits a uniaxial magnetism with the easy axis of magnetization parallel to [001] below the transition temperature, around 240 K. The saturated magnetization for the sintered $NaFe_3V_9O_{19}$ is 3.9 μ_B per formula unit. The transition temperature is an intermediate between those of NaV_6O_{11} (*13, 14*) and the magnetoplumbite ferrites (*9*) described above. Figure 3 shows the logarithmic resistivity of a sintered $NaFe_3V_9O_{19}$ sample as a function of temperature. The sintered sample showed semiconductor-like behavior and no anomaly was observed around the transition temperature. The resistivity at 299 K, 4.7 Ω cm, is close to that of La $Fe_{12}O_{19}$ at room temperature, 10 Ω cm (*10*). The resistivity data suggest that the magnetism of $NaFe_3V_9O_{19}$ can be described based on the localized *d*-electron model as in the case with the magnetoplumbite ferrites (*2–7*), but in contrast to NaV_6O_{11} (*14*). Further studies on a single crystal of Na $Fe_3V_9O_{19}$ are required to discuss the magnetism of this phase in detail and to answer the question of whether or not itinerant electrons play some roles in its magnetism.

References

1. W. D. TOWNES, J. H. FANG, AND A. J. PERROTTA, *Z. Kristallogr.* **125,** S.437 (1967).
2. J. S. VAN WIERINGEN, *Philips Tech. Rev.* **28,** 33 (1967).
3. R. L. STREEVER, *Phys. Rev.* **186,** 285 (1969).
4. F. K. LOTGERING, *J. Phys. Chem. Solids* **35,** 1633 (1974).
5. A. M. VAN DIEPEN AND F. K. LOTGERING, *J. Phys. Chem. Solids* **35,** 1641 (1974).
6. CH. SAUER, U. KÖBLER, AND W. ZINN, *J. Phys. Chem. Solids* **39,** 1197 (1978).
7. F. K. LOTGERING, P. R. LOCHER, AND R. P. VAN STAPELE, *J. Phys. Chem. Solids* **41,** 481 (1980).
8. R. S. TEBBLE AND D. J. CRAIK, "Magnetic Materials," Chap. 10, p. 362, Wiley, New York (1969).
9. A. AHARONI AND M. SHIEBER, *Phys. Rev.* **123,** 807 (1961).
10. V. L. MORUZZI AND M. W. SHAFER, *J. Am. Ceram. Soc.* **43,** 367 (1960).

11. M. E. de Roy, J. P. Besse, R. Chevalier, and M. Gasperin, *J. Solid State Chem.* **67,** 185 (1987).

12. Y. Kanke, K. Kato, E. Takayama-Muromachi, and M. Isobe, submitted for publication.

13. Y. Kanke, E. Takayama-Muromachi, K. Kato, and Y. Matsui, *J. Solid State Chem.* **89,** 130 (1990).

14. Y. Uchida, Y. Kanke, E. Takayama-Muromachi, and K. Kato, *J. Phys. Soc. Jpn.* **60,** 2530 (1991).

15. Y. Kanke, F. Izumi, E. Takayama-Muromachi, K. Kato, T. Kamiyama, and H. Asano, *J. Solid State Chem.*, **92,** 261 (1991).

16. *JCPDS* card 33-1340.

17. *JCPDS* card 38-470.

18. *JCPDS* card 26-976.

19. *JCPDS* card 26-983.