Growth and Characterization of $Fe_{1-x}M_xVO_4$ Single Crystals (M = Al, Cr, Co, Ga)

A. F. Bovina, I. A. Gudim, E. V. Eremin, and V. L. Temerov

Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia
e-mail: bezm@iph.krasn.ru

Abstract—Triclinic $Fe_{1-x}M_xVO_4$ single crystals (M = Al, Ga, Co, Cr) have been grown by the flux method from systems based on $PbO-V_2O_5$. Their crystallographic parameters are determined by powder X-ray diffraction. $Fe_{1-x}Ga_xVO_4$ single crystals (x = 0–0.3) with a volume more than $1 cm^3$ are grown using the seeding technique. The temperature and field dependences of magnetization and magnetic susceptibility of the grown $Fe_{1-x}Ga_xVO_4$ and $Fe_{1-x}Al_xVO_4$ single crystals (x = 0.3 in the solution−melt) are reported. It is shown that the magnetizations of these crystals exceed that of $FeVO_4$, and both of their antiferromagnetic phase transitions are shifted to lower temperatures.

INTRODUCTION

Oxide compounds with the simultaneous manifestation of magnetic and electric ordering and strong magnetoelectric interaction are the focus of the modern problem of searching for and synthesizing polyfunctional materials. Much attention is concentrated on the study of the microscopic nature of magnetoelectric coupling. In this context, the triclinic modification of $FeVO_4$ is of interest. The neutron diffraction study [1] revealed that this compound is an antiferromagnet at low temperatures; its magnetic structure is incommensurate: it is collinear in the range between $T_{N1} \sim 22$ and $T_{N2} \sim 15$ K and canted below $T_{N2} \sim 15$ K. It was shown that $FeVO_4$ is an intrinsic multiferroic at $T < 15$. When studying the magnetic structure and its influence on the magnetoelectric properties, the experiments with $FeVO_4$ single crystals, in which iron ions are partially replaced by other magnetic or nonmagnetic ions, seem to be important.

The growth of $FeVO_4$ single crystals encounters a number of difficulties. Therefore, in most works, the investigation of their properties has been performed on polycrystalline samples. Single crystals grown from proper melts [2, 3] had small sizes, and it was difficult to obtain samples with the necessary orientations. The low resistivity of samples ($\rho \sim 10^6 \Omega$ m at 300 K) [4] hindered measurements of the true electric polarization.

In this study, we determined the conditions and regimes for growing triclinic $Fe_{1-x}M_xVO_4$ phases (M = Al, Ga, Co, Cr) using the flux method from the $PbO-V_2O_5-Fe_2O_3-M_2O_3$ system. The temperature and field dependences of magnetization and magnetic susceptibility of grown $Fe_{1-x}Ga_xVO_4$ and $Fe_{1-x}Al_xVO_4$ single crystals with x = 0.3 in the melt are measured.

CRYSTAL GROWTH

The $PbO + pV_2O_5 + qFe_2O_3$ system was tested in our experiments on the growth of vanadate single crystals. It is established that, at temperatures below 1000°C, the crystallizable phases are either hematite α-Fe_2O_3 and/or trigonal $FeVO_4$ depending on the choice of the parameters p and q. With the parameters $p \sim 1.6$ and $q \sim 0.17$, $FeVO_4$ remains the only crystallizable phase in the temperature range of 500−750°C. This flux composition can be written in the binary form

$$(100 - n) \text{ wt } \%[PbO + 1.43V_2O_5] + n \text{ wt } \% FeVO_4,$$

where n is the concentration of crystal-forming oxides corresponding to the $FeVO_4$ stoichiometry. The concentration dependence of the saturation temperature, $T_{sat}(n)$, of this solution−melt is shown in Fig. 1.

The flux density equal to ~4 g/cm^3 is higher than that of grown crystals (~3.5 g/cm^3). Therefore, crystallization takes place in the near-surface region of the melt.

The possibility of growing $Fe_{1-x}M_xVO_4$ single crystals (M = Al, Ga, Cr, Co) by the flux method was tested based on this system. The composition prepared to this end can be described by the formula $(100 - n)$ wt % $[PbO + 1.43V_2O_5] + n$ wt % $Fe_{1-x}M_xVO_4$. Substituted crystals were subsequently grown from the same flux with a stepwise increase in x by Δx = 0.1−0.15. The largest x values and the concentrations of crystal-forming oxides tested in the experiments are
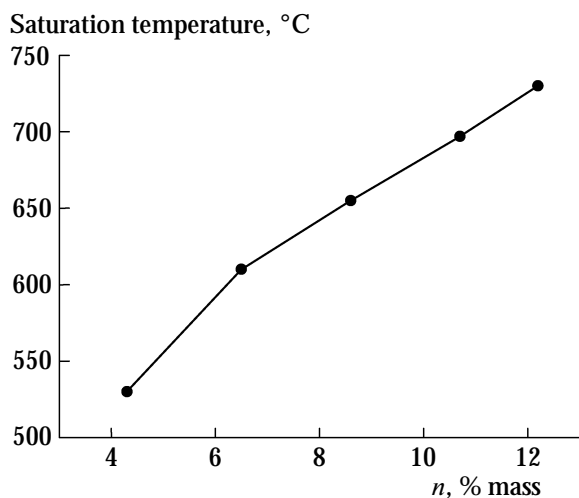
Saturation temperature, °C

Fig. 1. Dependence of saturation temperature of flux on $FeVO_4$ concentration.

Fig. 2. $FeVO_4$ (right) and $Fe_{0.8}Ga_{0.2}VO_4$ single crystals.

listed in Table 1. In all cases, the saturation temperatures were within 700−730°C.

To grow large crystals, we used the initial composition 89.3 wt % [PbO + 1.43V_2O_5] + 10.7 wt % $FeVO_4$ with a mass of 1500 g. The composition was prepared by heating a mixture of sifted oxides to $T = 900$°C in a Pt crucible 90 mm in diameter and 90 mm high. The crucible was placed in a crystallization furnace, where the temperature was reduced from the crucible bottom with a vertical gradient of 1−2°C/cm. Flux was homogenized at $T = 900$°C for 24 h. Within this period, the flux was stirred by a Pt mixer that rotated at a rate of 40 rpm. The saturation temperature $T_{sat} \sim$ 700°C was refined in the range of ±2°C by means of

small probe crystals, which were obtained preliminarily from the same flux under the conditions of spontaneous crystallization on a rotating Pt rod.

Then, a rod with a seed fixed on its end was suspended over themelt at $T = T_{sat} + 5$°C and, 20 min later, the seed was immersed in the melt to a depth of 1 mm. The temperature was reduced to $T = T_{sat} − 1$°C, and the rod started to rotate at a rate of 40 rpm. Further crystal growth occurred with a programmable reduction of the temperature by 1−6°C/day so that the growth rate did not exceed 1 mm/day. The growth lasted 10−20 days. When it was ended, the crystal was lifted above the surface of the melt and cooled to room temperature, along with the switched-off furnace. After replenishment with crystal-forming oxides in an amount corresponding to the mass of the extracted crystals, the flux was used repeatedly. To grow gallium-substituted iron vanadates, the flux was replenished with oxides according to the $Fe_{1-x}Ga_xVO_4$ stoichiometry. The grown $FeVO_4$ single crystals 14 g in mass and $Fe_{1-x}Ga_xVO_4$ single crystals ($x = 0.2$ in the flux) 6.5 g in mass are shown in Fig. 2.

Table 1. Largest values of x and concentrations of crystal-forming oxides sampled in experiments

M	Al	Ga	Cr	Co
x	0.7	0.3	0.1	0.3
n	16.9	12.7	11.2	12.6

Table 2. Lattice parameters of the grown crystals in dependence of the content of substituting element in the flux

M	x (in flux)	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg
		6.709(3)	8.045(3)	9.340(3)	96.43(2)	106.85(1)	101.49(2)
		6.728(5)	8.038(8)	9.338(5)	96.621	105.730	101.140
Co	0.2	6.750	8.032	9.340	97.135	105.760	100.976
Al	0.3	6.744	8.023	9.337	97.097	106.532	101.189
Al	0.6	6.698	8.432	9.342	96.145	107.080	101.978
Cr	0.1	6.716	8.099	9.314	97.208	106.022	101.367
Ga	0.15	6.751	7.671	9.276	105.033	100.226	97.457
Ga	0.3	6.727	7.657	9.283	105.128	100.230	97.504

* Data of [3].
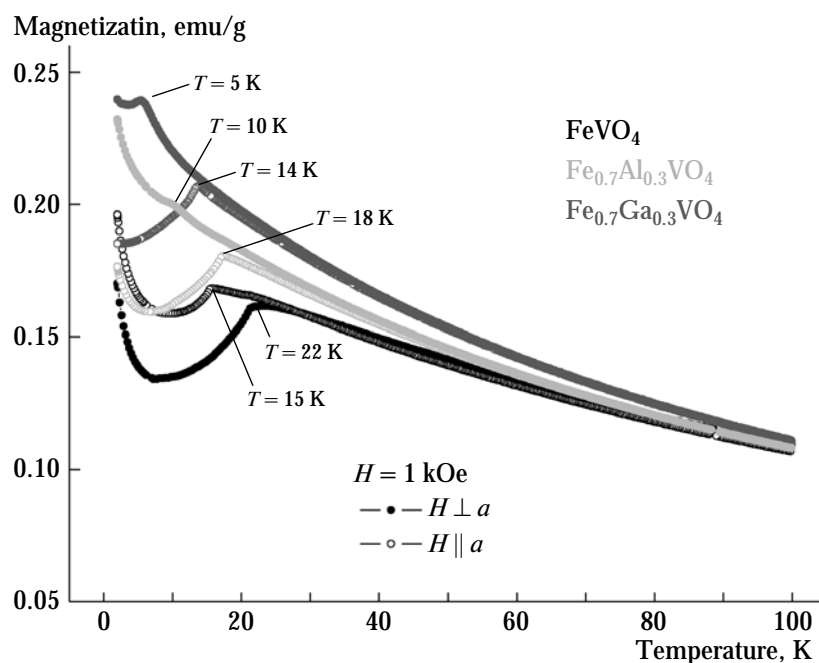
Magnetizatin, emu/g

Fig. 3. Temperature dependences of magnetization for $FeVO_4$, $Fe_{0.7}Ga_{0.3}VO_4$, and $Fe_{0.7}Al_{0.3}VO_4$ measured in a magnetic field of 1 kOe (open circles) along and (filled circles) normally to the a axis.

CHARACTERIZATION

The lattice parameters of the crystals measured by powder X-ray diffraction in the dependence of the content of the substituent in the flux are listed in Table 2.

The X-ray diffraction analysis confirmed that these crystals belong to the triclinic system with a space group $P1$. The lattice parameters of nonsubstituted $FeVO_4$ grown from the $PbO-V_2O_5-Fe_2O_3$ composition were close to the corresponding parameters of $FeVO_4$ [3] grown from the $Fe_2O_3-V_2O_5$ system. The largest deviations in the lattice parameters are observed for gallium-substituted iron vanadates.

The dc resistivity was measured by the two-electrode method to be $\sim 10^9\ \Omega \cdot m$ (300 K) for $FeVO_4$ and $Fe_{1-x}M_xVO_4$ crystals (M = Al, Ga, Cr) and $\sim 10^{12}\ \Omega\, m$ (300 K) for $Fe_{0.8}Co_{0.2}VO_4$.

The magnetic measurements were carried out for $FeVO_4$, $Fe_{0.7}Ga_{0.3}VO_4$, and $Fe_{0.7}Al_{0.3}VO_4$ crystals. Hereinafter, the contents of substituents are given based on the ratio of crystal-forming oxides in the flux. The measurements were carried out along the crystal a axis and normally to it on the Physical Properties Measurement System (Quantum Design) in the temperature range of 2–300 K and in magnetic fields up to 9 T.

The temperature dependences of magnetization are shown in Fig. 3. It can be seen that the magnetization values at the aforementioned replacement of iron with nonmagnetic gallium or aluminum ions exceed that of $FeVO_4$ at the same temperatures. Moreover, the antiferromagnetic phase transitions, which occur at T_{N1}

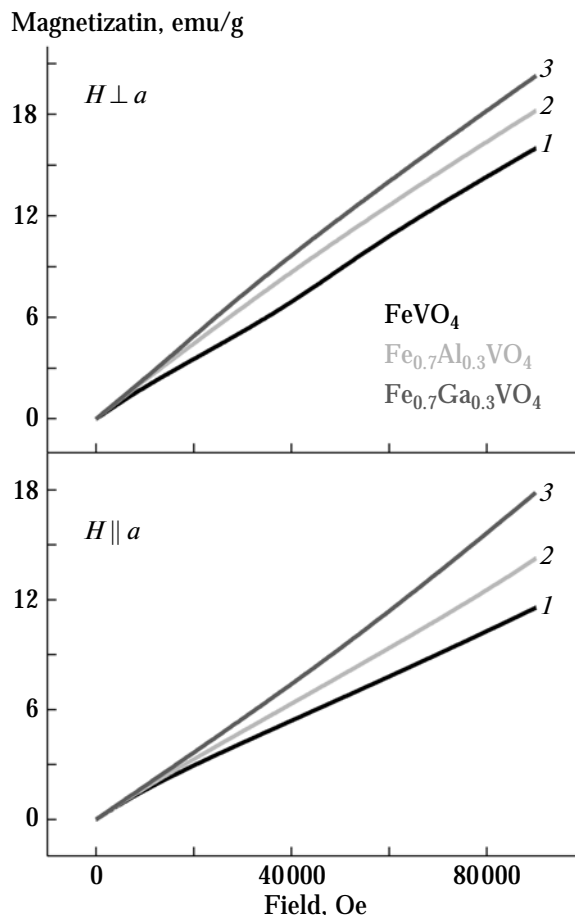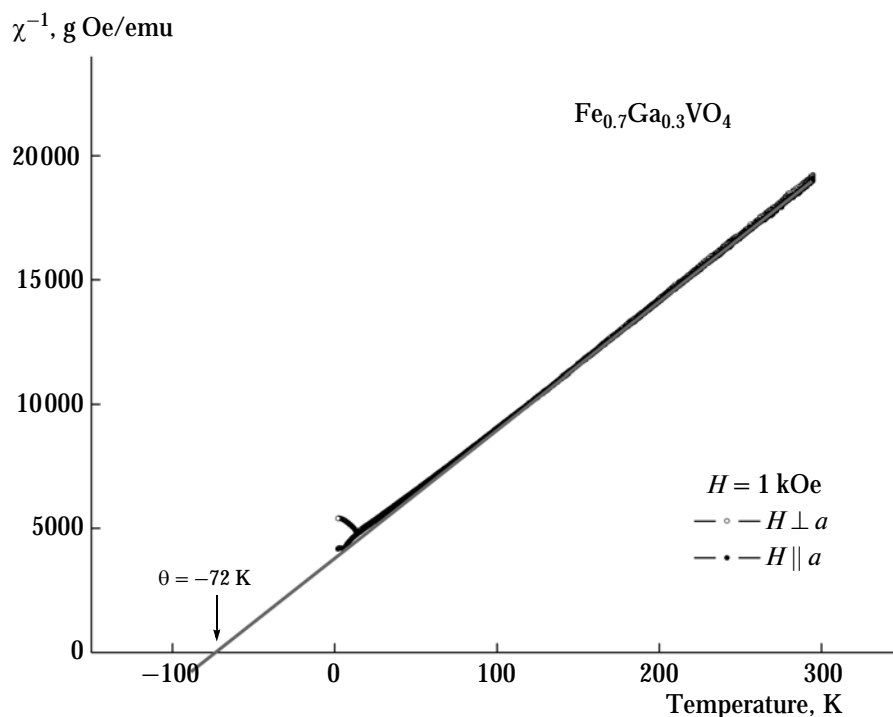Magnetizatin, emu/g

Fig. 4. Magnetization at $T = 2$ K as a function of magnetic field applied along and normally to the a axis for (*1*) $FeVO_4$, (*2*) $Fe_{0.7}Al_{0.3}VO_4$, and (*3*) $Fe_{0.7}Ga_{0.3}VO_4$ crystals.

χ^{-1}, g Oe/emu

Fig. 5. Temperature dependences of inverse magnetic susceptibility ($1/\chi$) for $Fe_{0.7}Ga_{0.3}VO_4$ measured in a magnetic field of 1 kOe along (open circles) and normally (filled circles) to the *a* axis.

($M(T)$ peak for $H \perp a$) and T_{N2} ($M(T)$ peak for $H \parallel a$) [1], are shifted to lower temperatures. In this case, the range $\Delta T = T_{N1} - T_{N2}$ remains almost the same as for $FeVO_4$.

It also follows from Fig. 4, where the field dependences of the magnetization $M(H)$ at $T = 2$ K are shown, that the magnetic moment for the above-mentioned substituted iron vanadates is larger than that for $FeVO_4$.

The temperature dependences of the inverse susceptibility ($1/\chi$) at $H = 1$ kOe for $Fe_{0.7}Ga_{0.3}VO_4$ are shown in Fig. 5. The similar behavior of magnetic susceptibility was observed for $FeVO_4$ and $Fe_{0.7}Al_{0.3}VO_4$. Above the temperature $T \approx 50$ K, these dependences obey the Curie–Weiss law. In this case, the found values of the Curie temperature, $T_C = -82$ K for $Fe_{0.7}Al_{0.3}VO_4$ and $T_C = -72$ K for $Fe_{0.7}Ga_{0.3}VO_4$, shift to higher temperatures than $T_C = -102$ K for $FeVO_4$.

CONCLUSIONS

The conditions and regimes of growing $Fe_{1-x}M_xVO_4$ crystals (M = Al, Ga, Co, Cr) by the flux method from compositions based on $PbO-V_2O_5$ using the seeding technique were determined. The lattice parameters were determined for the single crystals grown. The resistivity reaches $\sim 10^9$ Ω m (300 K) for $FeVO_4$ and $Fe_{1-x}M_xVO_4$ with M = Al, Ga, Cr and $\sim 10^{12}$ Ω m (300 K) for $Fe_{0.8}Co_{0.2}VO_4$. It was established that the magnetization of $Fe_{1-x}Ga_xVO_4$ and $Fe_{1-x}Al_xVO_4$ with $x \approx 0.3$ is larger than that of $FeVO_4$, and the temperatures of magnetic phase transitions (T_{N1} and T_{N2}) are shifted to lower temperatures.

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