Journal of Alloys and Compounds 509 (2011) 8153–8157

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Magnetic properties of a new iron lead vanadate $Pb_2FeV_3O_{11}$

N. Guskos[a,b], J. Typek[b,*], G. Zolnierkiewicz[b], R. Szymczak[c], P. Berczynski[b], K. Wardal[b], A. Blonska-Tabero[d]

[a] Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, 15 784 Zografos, Athens, Greece
[b] Institute of Physics, West Pomeranian University of Technology, Al. Piastow 48, 70-311 Szczecin, Poland
[c] Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 36/42, Warszawa, Poland
[d] Department of Inorganic and Analytical Chemistry, West Pomeranian University of Technology, Al. Piastow 42, 70-065 Szczecin, Poland

ARTICLE INFO

Article history:
Received 6 April 2011
Received in revised form 26 May 2011
Accepted 30 May 2011
Available online 6 June 2011

Keywords:
EPR
Vanadates
Magnetic susceptibility

ABSTRACT

Temperature dependence of dc/ac magnetization and electron paramagnetic resonance (EPR) spectra of $Pb_2FeV_3O_{11}$ iron lead vanadate has been investigated. The dc magnetic measurements have shown the presence of antiferromagnetic interactions with Curie–Weiss temperature, $T_{CW} = -15.2$ K, in the high temperatures range while the field cooled (FC) magnetization revealed a maximum at $T_N = 2.5$ K which coincides with a long range magnetic ordering. Temperature dependence of χ' has shown a maximum at the same temperature. EPR spectrum of $Pb_2FeV_3O_{11}$ at room temperature is dominated by nearly symmetrical, very intense and broad resonance line centered at $g_{eff} \sim 2.0$ that could be attributed to the correlated system of iron ions. The temperature dependence of magnetic resonance parameters (amplitude, *g*-factor, linewidth, integrated intensity) has been determined in the 4–300 K range and it suggests the existence of short range correlated spin system up to high temperatures. The temperature dependence of the amplitude of the resonance line has shown a pronounced maximum at 12.5 K that indicates on the existence of two subsystems of weakly and strongly coupled iron pairs. Comparison of dc magnetic susceptibility and EPR integrated intensity points to the presence of correlated spin agglomerates that play an important role in determination of the magnetic response of $Pb_2FeV_3O_{11}$.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Multicomponent vanadates M–Fe–V–O (M(II) = Mg, Zn, Mn, Cu, Ni and Co) exhibit very interesting physical (structural, magnetic and transport) and catalytic properties [1–14]. They belong to a group of useful catalysts used for the reaction of partial oxidation of organic compounds. Structural disorder, introduced by replacement of some magnetic ions in the sublattice of M(II) cations could results in an intense magnetic competition and frustration phenomena [9,10,15,16]. The above systems have displayed a very strong antiferromagnetic (AFM) interaction with very high values of the Curie–Weiss temperature, especially in compounds with Co(II) and Mn(II) magnetic ions.

Magnetic resonance measurements have shown that the above systems are approaching the phase with a long range magnetic order at high temperatures but dc magnetic susceptibility study has not shown the existence of such state even down to 3 K. The crystal structure of the system with Ni(II) magnetic ion at the cation position is not known and in this compound very complicated magnetic multiphase aggregate states are observed [17,18]. The temperature and frequency dependence of high frequency electron paramagnetic resonance (HF-EPR) spectra have shown that in $Mn_3Fe_4V_6O_{24}$ compound there is the coexistence of AFM with ferromagnetic (FM) interactions [10]. Recently, a new $Pb_2FeV_3O_{11}$ multicomponent vanadate was synthesized which crystallizes in higher crystallographic symmetry (monoclinic) than previously investigated $M_2FeV_3O_{11}$ (M(II) = Co, Mg and Zn) compounds (triclinic) [19].

The aim of this work is to study magnetic properties of a new $Pb_2FeV_3O_{11}$ lead vanadate in which the Pb^{2+} ion have a much greater radius than cations in other M(II) = Co, Mg, Ni, Zn vanadates. Dc/ac magnetic susceptibility and EPR methods will be employed. The obtained results will be compared with similar studies made on other $M_2FeV_3O_{11}$ vanadates.

2. Experimental

$Pb_2FeV_3O_{11}$ multicomponent vanadate was synthesized from an equimolar mixture of iron(III) orthovanadate(V) and lead(II) pyrovanadate(V): $FeVO_4 + Pb_2V_2O_7 = Pb_2FeV_3O_{11}$. Iron(III) orthovanadate(V) was obtained as a result of heating of equimolar mixture of Fe_2O_3 and V_2O_5 in three stages: 560 °C (20 h) + 590 °C (20 h × 2). Synthesis of lead(II) pyrovanadate(V) was performed during heating the stoichiometric mixture of $Pb(NO_3)_2$ and V_2O_5 in the following stages: 430 °C (20 h × 2) + 600 °C (20 h). The reactions were carried out by the conventional

---

[*] Corresponding author.
E-mail address: typjan@zut.edu.pl (J. Typek).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.05.114

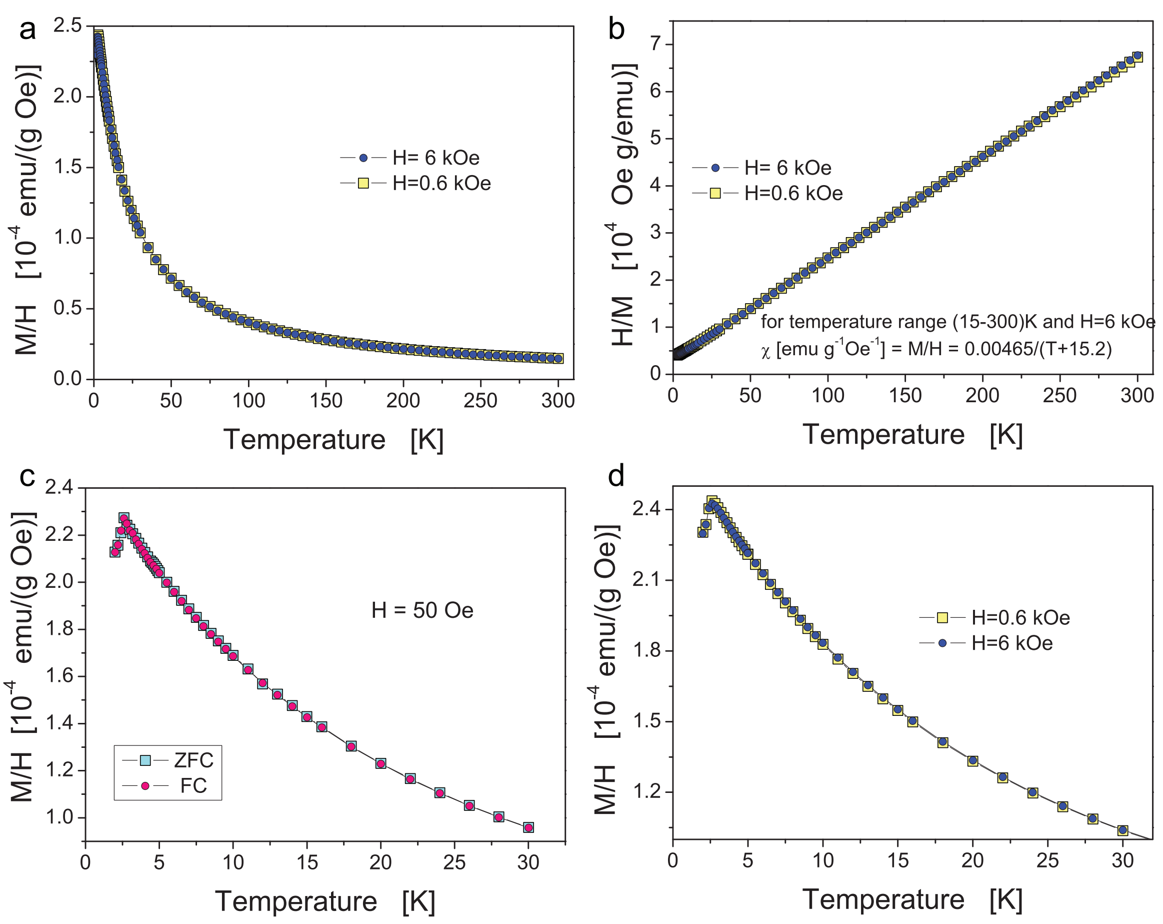

Fig. 1. Temperature dependence of the dc magnetic susceptibility (a), inverse magnetic susceptibility (b), low temperature range for $H = 50$ Oe (c) and $H = 0.6$ kOe, $H = 6$ kOe (d).

method of calcination [19]. Appropriate portions of reacting substances were homogenized by grinding and heated in air during several stages until a monophase sample was obtained or until the composition of the samples did not change after two consecutive heating stages. $Pb_2FeV_3O_{11}$ crystallizes in monoclinic symmetry with the following lattice parameters: $a = 0.56414(7)$ nm, $b = 0.74970(9)$ nm, $c = 0.7497(9)$ nm, $\beta = 81.72(1)^\circ$, $V = 0.4765$ nm^3 and $\rho_{calc} = 5.579$ g/cm^3 [19]. The values of lattice parameters for $Pb_2FeV_3O_{11}$ are essentially smaller than for other $M_2FeV_3O_{11}$ compounds with triclinic symmetry (M = Zn, Mg) while its density is higher and the melting temperature (650 °C) is essentially smaller [11,12].

The dc susceptibility measurements were carried out in the 2–300 K temperature range using an MPMS-5 SQUID magnetometer and in magnetic fields up to 50 kOe in the zero-field-cooled (ZFC) and field-cooled (FC) modes. The real χ' as well as imaginary χ'' parts of ac magnetic susceptibility were measured using mutual inductance method in an ac magnetic field of 0–10 kHz frequency range and with amplitude not exceeding 1 Oe.

The EPR spectra were recorded using a standard X-band Bruker E 500 spectrometer ($\nu = 9.45$ GHz) with magnetic field modulation of 100 kHz. The magnetic field was scaled with a NMR magnetometer. The measurements were performed in the temperature range from 3 to 290 K using an Oxford helium flow cryostat.

3. Experimental results and discussions

3.1. Dc and ac magnetic measurements

Fig. 1 shows the temperature dependence of dc magnetic susceptibility (χ) and its inverse (χ^{-1}) for the whole temperatures range as well as the magnetic susceptibility at low temperatures, obtained from dc magnetization measurements of $M_{ZFC}(T)$ for different values of an applied magnetic field. The temperature dependence of magnetic susceptibility is displaying the Curie–Weiss behavior, $\chi(T) = C/(T - T_{CW})$. The following value of the Curie–Weiss temperature is obtained: $T_{CW} = -15.2(1)$ K indicating domination of AFM interaction as shown by the negative sign of this constant. This value is significantly smaller in comparison with similar systems displaying lower symmetry $M_2FeV_3O_{11}$ (M(II) = Mg and Zn), for which $T_{CW} = -50(1)$ K (for $Mg_2FeV_3O_{11}$) and $T_{CW} = -58(1)$ K (for $Zn_2FeV_3O_{11}$) was observed [7,8]. The Curie–Weiss fit to $\chi^{-1}(T)$ data for $Pb_2FeV_3O_{11}$ yields an effective magnetic moment of $5.46(1)\mu_B$ per formulae unit. It is similar to what was obtained for samples with Zn(II) and Mg(II) ions at cation position.

At $T = 2.5$ K the dc susceptibility in FC and ZFC modes exhibits the same maximum for different applied magnetic fields (Fig. 1c and d) and no branching of FC and ZFC curves in AFM phase. This is rather different to what was registered for similar $Zn_2FeV_3O_{11}$ and $Mg_2FeV_3O_{11}$ compounds. For those compounds the splitting of the FC and ZFC magnetization curves was observed, signalling the onset of irreversibility. At higher magnetic fields ($H > 100$ Oe), the maximum in magnetization became gradually smeared out, while the irreversibility onset shifted to lower temperatures, both indicative of a spin freezing transition. Such behavior suggested significant spin frustration in the magnetic system as well as appreciable AFM correlations in the paramagnetic phase. In the presently studied $Pb_2FeV_3O_{11}$ compound the frustration phenomena seems to play a significantly smaller role. This is presumably due to the higher crystallographic symmetry of this material.

Fig. 2 shows the field dependence of the isothermal dc magnetization $M(H)$ at 2 K and 5 K. The low magnetization at low temperatures, persistent up to 50 kOe, asserts a strong AFM coupling and the concurrent compensation of some fraction of isolated trivalent iron ions in the high spin $^6S_{5/2}$ ground state. Below 2.5 K the magnetic spin correlated system is in the long-range ordered AFM state. Small curvature of the $M(H)$ curves at low temperatures complies qualitatively with the presence of a small fraction of relatively uncompensated spins or AFM clusters with reduced energy gap at low temperatures.

Fig. 3 shows the temperature dependence of the real and imaginary part of the ac susceptibility. This quantity was measured on warming up the sample after cooling down in zero magnetic field. The χ' curve shows pronounced maximum at $T_f = 2.5$ K derived at 0 Hz, 1 Hz as well as 10 kHz so it does not depend on frequency. The observed peak at 2.5 K is characteristic of the transition of the correlated spin system to the AFM state.

3.2. EPR measurements

Fig. 4 presents the EPR spectra at X-band for the $Pb_2FeV_3O_{11}$ compound registered at different temperatures in the 4–300 K range. As could be easily noticed the EPR line varies strongly with temperature what is reflected in considerable thermal dependence of the EPR line parameters: amplitude, resonance field, linewidth

Download English Version:

https://daneshyari.com/en/article/1616819

Download Persian Version:

https://daneshyari.com/article/1616819

Daneshyari.com