

University of Massachusetts Amherst

From the Selected Works of Kevin R. Kittilstved

April, 2005

Chemical Manipulation of High-TC Ferromagnetism in ZnO Diluted Magnetic Semiconductors

Kevin R. Kittilstved, *University of Massachusetts - Amherst*

D. R Gamelin

N. S Norberg



Available at: https://works.bepress.com/kevin_kittilstved/6/

Chemical Manipulation of High- T_C Ferromagnetism in ZnO Diluted Magnetic Semiconductors

Kevin R. Kittilstved, Nick S. Norberg, and Daniel R. Gamelin

Department of Chemistry and Center for Nanotechnology, University of Washington, Seattle, WA 98195-1700, USA
(Received 6 November 2004; revised manuscript received 1 December 2004; published 15 April 2005)

We report the use of targeted p - and n -type chemical perturbations to manipulate high- T_C ferromagnetism in $\text{Mn}^{2+}:\text{ZnO}$ and $\text{Co}^{2+}:\text{ZnO}$ in predictable and reproducible ways. We demonstrate a clear correlation between nitrogen and high- T_C ferromagnetism for $\text{Mn}^{2+}:\text{ZnO}$ and an inverse correlation for $\text{Co}^{2+}:\text{ZnO}$, both as predicted by recent theoretical models. These chemical perturbations reveal rich possibilities for exerting external control over high- T_C spin ordering in diluted magnetic semiconductors.

DOI: 10.1103/PhysRevLett.94.147209

PACS numbers: 75.50.Dd, 61.72.Vv, 75.50.Pp, 75.50.Tt

The technological importance of ZnO has been bolstered by recent successes in the preparation of low-resistivity p -type ZnO, which makes fabrication of ZnO homojunction devices such as light-emitting and laser diodes possible [1]. One technology in which p -type ZnO could have a major impact is the emerging field of spin electronics based on diluted magnetic semiconductors (DMSs) [2]. DMS ferromagnetism above room temperature is an essential criterion for practical semiconductor spintronics device applications, and theoretical models have identified p -type $\text{Mn}^{2+}:\text{ZnO}$ as a leading candidate for high- T_C ferromagnetism [3–5]. Since Mn^{2+} doping into ZnO does not itself generate p -type carriers, p -type defects must be introduced deliberately by other routes. In this Letter, we report that nitrogen-containing molecules can be used to manipulate high- T_C ferromagnetism in ZnO DMSs. This effect is attributed to the generation of uncompensated p -type defects by analogy to previous successful syntheses of p -type ZnO [1]. A clear correlation between nitrogen addition and strong 300 K ferromagnetism in $\text{Mn}^{2+}:\text{ZnO}$ is observed, whereas a clear inverse correlation is observed for $\text{Co}^{2+}:\text{ZnO}$, a DMS proposed to require n -type defects for ferromagnetism [4,6,7]. These results provide strong experimental evidence of intrinsic carrier-mediated high- T_C ferromagnetism in these DMSs and suggest new opportunities for using *ex situ* perturbations to advance spin-based information processing technologies.

Despite clear theoretical predictions [3–5], $\text{Mn}^{2+}:\text{ZnO}$ ferromagnetism remains poorly understood experimentally. Several authors have reported the absence of ferromagnetism in $\text{Mn}^{2+}:\text{ZnO}$ at any temperature [8], but others have reported ferromagnetism with T_C below room temperature [9]. Following the first claim of weak room-temperature ferromagnetism in $\text{Mn}^{2+}:\text{ZnO}$ [ferromagnetic saturation moment of M_S (300 K) $\approx 0.16\mu_B/\text{Mn}^{2+}$] [10], ferromagnetism was observed in $\text{Mn}^{2+}:\text{ZnO}$ films grown on GaAs annealed above 500 °C that appeared to correlate with the development of p -type conductivity [11], but ferromagnetism near room temperature was also claimed for n -type $\text{Mn}^{2+}:\text{ZnO}$ [12]. Most recently, ferromagnetism attributed earlier to $\text{Mn}^{2+}:\text{ZnO}$ was suggested to

arise instead from phase-segregated impurities such as Zn-doped Mn_2O_3 [13] or Mn_3O_4 [14].

We recently reported strong high- T_C ferromagnetism in 0.20% $\text{Mn}^{2+}:\text{ZnO}$ prepared by a direct chemical synthesis route in which $\text{Mn}^{2+}:\text{ZnO}$ colloids were used as precursors for spin coating nanocrystalline films [15]. To explain the strong ferromagnetism [M_S (300 K) = $1.35\mu_B/\text{Mn}^{2+}$], we hypothesized that calcination of the surface-capping amines left behind nitrogen that could serve as a p -type defect [15]. To test this hypothesis, we have now performed the split-batch experiment described below. High-quality $\text{Mn}^{2+}:\text{ZnO}$ nanocrystals (6 ± 1 nm diameter) were prepared as described previously [15]. After growth in dimethylsulfoxide (DMSO), the nanocrystals were precipitated with ethyl acetate and washed with heptane. Half of the nanocrystals were then heated to 145 °C for 30 min 2 times in 9:1 w/w trioctylphosphine oxide (TOPO, $R_3\text{PO}$, $R = \text{C}_8\text{H}_{17}$)/stearyl phosphate, precipitated and washed with ethanol, and resuspended in toluene to form a clear suspension of oxygen-capped (O-capped) nanocrystals. For the other half, the same procedure was performed using dodecylamine ($R'\text{NH}_2$, $R' = \text{C}_{12}\text{H}_{25}$) instead of TOPO, yielding a clear suspension of amine-capped (N-capped) nanocrystals. Detailed magnetic and spectroscopic characterization indicated homogeneous distribution of substitutional paramagnetic Mn^{2+} in wurtzite ZnO [15]. The O- and N-capped colloids were then spin coated into ~ 1 μm thick films on fused-silica substrates as described previously [15], with aerobic calcination at 500 °C for 2 min between coats (~ 20 coats total). Microscopy images show these films to be relatively thick but porous networks of sintered ZnO crystallites (see [16]). Mn^{2+} concentrations were quantified by atomic emission spectrophotometry. Figure 1(a) shows magnetization data for nanocrystalline films prepared from O- and N-capped 0.20% $\text{Mn}^{2+}:\text{ZnO}$ colloids, corrected for the diamagnetism of the sample holder and substrate. The two films possessed remarkably different magnetic properties. Whereas the film prepared from O-capped nanocrystals was paramagnetic at all temperatures and showed little measurable magnetization at

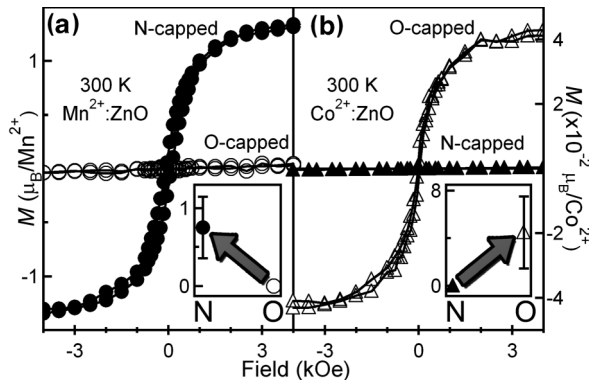


FIG. 1. 300 K magnetization vs field loops for (a) 0.20% $\text{Mn}^{2+}:\text{ZnO}$ and (b) 3.5% $\text{Co}^{2+}:\text{ZnO}$ films prepared from N-capped (\bullet , \blacktriangle) or O-capped (\circ , \triangle) colloids as described in the text. Insets: statistics for 300 K ferromagnetic saturation moments obtained from ≥ 10 independent films for each case. Hysteresis temperature dependence data are provided in [16].

300 K, the film prepared from N-capped nanocrystals was strongly ferromagnetic with $T_C > 350$ K and a room-temperature coercivity of 92 ± 7 Oe (see [16]).

The split-batch experiment was repeated for several $\text{Mn}^{2+}:\text{ZnO}$ films of each type (O and N capped), and the resulting statistics are shown in the inset to Fig. 1(a). Three of the 10 O-capping experiments used acetate (CH_3COO^-) instead of TOPO and three of the 13 N-capping experiments used trioctylamine ($R_3\text{N}$) instead of $R'\text{NH}_2$. Without exception, the O-capped $\text{Mn}^{2+}:\text{ZnO}$ nanocrystals yielded paramagnetic films [$M_S(300\text{ K}) = 0.00 \pm 0.00 \mu_B/\text{Mn}^{2+}$] and the N-capped nanocrystals yielded ferromagnetic films [$M_S(300\text{ K}) = 0.75 \pm 0.40 \mu_B/\text{Mn}^{2+}$]. The same dependence on nitrogen was found for polycrystalline powders (see [16]). Importantly, by starting with uniformly doped paramagnetic 0.20% $\text{Mn}^{2+}:\text{ZnO}$ [15] rather than with segregated manganese and zinc oxides, scenarios involving phase segregation of ferromagnetic manganese oxides [13,14] are rendered highly improbable, particularly since this low Mn^{2+} concentration is approximately 2 orders of magnitude below the solid solubility of Mn^{2+} in ZnO [17]. Consistent with this consideration, only wurtzite ZnO was observed in x-ray diffraction of the ferromagnetic films (see [16]). Similarly, quantitative magnetic measurements show no evidence of any Mn^{2+} segregation induced by calcination (see [16]). Because of the relatively large ferromagnetic saturation moments per Mn^{2+} and the very low Mn^{2+} concentration, the ferromagnetism in Fig. 1(a) must involve a long-range magnetic exchange mechanism.

As a control, the same split-batch experiment was performed for $\text{Co}^{2+}:\text{ZnO}$, a DMS for which growing evidence suggests that the introduction of n -type defects promotes 300 K ferromagnetism [4,6,7]. The chemical trend observed for $\text{Co}^{2+}:\text{ZnO}$ was exactly opposite that of $\text{Mn}^{2+}:\text{ZnO}$. The O-capped $\text{Co}^{2+}:\text{ZnO}$ nanocrystals [18] consistently yielded films showing 300 K ferromagnetism, albeit weak, whereas the N-capped nano-

crystals yielded exclusively paramagnetic films [Fig. 1(b)]. The coercivity of the ferromagnetic signal was again small (see [16]). The inset of Fig. 1(b) shows statistics from 10 films prepared using O-capped nanocrystals [$M_S(300\text{ K}) = 0.045 \pm 0.030 \mu_B/\text{Co}^{2+}$] and 10 films prepared using N-capped nanocrystals [$M_S(300\text{ K}) = 0.00 \pm 0.00 \mu_B/\text{Co}^{2+}$]. Notably, the oxidative synthesis and spin coating conditions preclude the formation of cobalt metal, and these data therefore refute suggestions that ferromagnetism in $\text{Co}^{2+}:\text{ZnO}$ arises only from precipitation of cobalt metal [19]. Instead, the data in Figs. 1(a) and 1(b) offer clear evidence for the importance of factors other than the transition-metal dopants in governing the magnetism of Mn^{2+} - and Co^{2+} -doped ZnO .

The photoluminescence (PL) and infrared (IR) absorption spectra of ZnO colloids in Fig. 2 reveal that surface capping strongly influences the ZnO defect characteristics. Undoped ZnO was used for these measurements since $\text{Mn}^{2+}:\text{ZnO}$ and $\text{Co}^{2+}:\text{ZnO}$ both possess sub-bandgap charge-transfer states that introduce effective pathways for nonradiative relaxation [15,18]. Figure 2(a) shows absorption and PL spectra of as-prepared ZnO colloids suspended in DMSO. The PL spectrum is dominated by a characteristic broad green emission band centered at 2.3 eV that is closely associated with surface defects including OH^- [20]. Importantly, OH^- is also a potential n -type defect in ZnO [21]. The green emission intensity is reduced considerably by both TOPO and $R'\text{NH}_2$ surface-capping procedures [Fig. 2(b) and 2(c)], suggesting reduced surface OH^- concentrations. This conclusion is verified by the reduced OH^- stretching intensities at 0.425 eV in the IR absorption spectra of drop-cast films of both TOPO- and $R'\text{NH}_2$ -capped nanocrystals [Fig. 2(e) and 2(f)] relative to that of the as-prepared nanocrystals [Fig. 2(d)]. Thus, ZnO surface defects that may otherwise introduce n -type carriers to the spin-coated films are suppressed by both

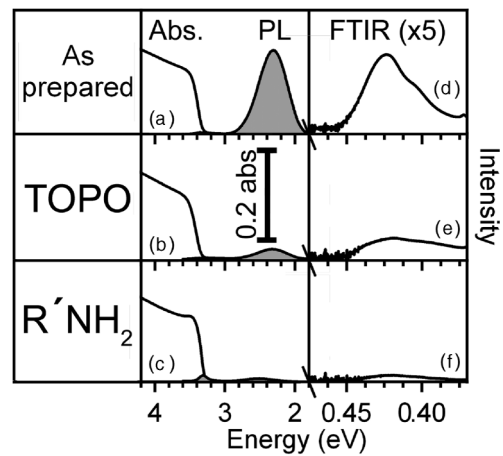


FIG. 2. 300 K electronic absorption, photoluminescence (shaded), and IR absorption spectra of ZnO nanocrystals. (a) As prepared, suspended in DMSO. (b) O capped (TOPO), suspended in heptane. (c) N capped (dodecylamine), suspended in 2:1 heptane : EtOH. (d)–(f) Same as (a)–(c), on NaCl plates.

TOPO and amine surface-capping procedures. Amine capping additionally provides a ready source of nitrogen directly coordinated to surface Zn^{2+} ions prior to calcination. We hypothesize that ligand calcination incorporates Zn^{2+} -bound nitrogen into the ZnO lattice at crystallite fusion interfaces. The similarity of the nitrogen sources employed in our experiments ($R_3\text{N}$ and $R'\text{NH}_2$) to those previously used for the preparation of p -type ZnO (e.g., NH_3 , NH_4NO_3 , N_2O , NO , and Zn_3N_2) [1,22,23] therefore strongly suggests that the ferromagnetism shown in Fig. 1(a) arises from the introduction of uncompensated p -type defects, tentatively proposed to be N_O by analogy to other N-doped ZnO studies [1]. Regrettably, attempts to measure the Hall effect or Seebeck coefficients for the nanocrystalline films have failed because of the high resistivities ($> 10^8 \Omega \text{ cm}$) typical of such films.

Magnetic ordering in $\text{Mn}^{2+}:\text{ZnO}$ and $\text{Co}^{2+}:\text{ZnO}$ could also be manipulated by *ex situ* n - or p -type perturbations. For the p -type perturbation, N-containing molecules were adsorbed directly onto the surfaces of the films. When 0.1 mL of 0.5M $\text{Zn}(\text{NO}_3)_2/R'\text{NH}_2$ (1:1) in ethanol was dropped onto a film of $\text{Mn}^{2+}:\text{ZnO}$ prepared from N-capped nanocrystals, followed by solvent evaporation and aerobic calcination at 500 °C for 2 min, the film's 300 K saturation moment increased 300% [Fig. 3(a)]. The same experiment performed on a film of $\text{Co}^{2+}:\text{ZnO}$ prepared from O-capped nanocrystals reduced its 300 K saturation moment by 60% [Fig. 3(b)]. No changes in the magnetism of either $\text{Mn}^{2+}:\text{ZnO}$ or $\text{Co}^{2+}:\text{ZnO}$ occurred in control experiments using the identical procedure omitting only the $\text{Zn}(\text{NO}_3)_2/R'\text{NH}_2$. These control experiments eliminate the possibility that the ferromagnetism arises solely from heat or the introduction of carbon.

For the *ex situ* n -type perturbation, the films were exposed to Zn vapor, shown previously to increase ZnO

n -type conductivity likely by incorporation of the shallow donor, interstitial zinc (Zn_i) [24]. As reported recently [7], Zn vapor diffusion into paramagnetic $\text{Co}^{2+}:\text{ZnO}$ activated room-temperature ferromagnetism [Fig. 3(d)]. In contrast, Zn vapor diffusion into ferromagnetic $\text{Mn}^{2+}:\text{ZnO}$ prepared from N-capped nanocrystals largely quenched its ferromagnetism [Fig. 3(c)] and was accompanied by a concomitant increase in Mn^{2+} paramagnetism (data not shown). Control experiments using ZnO lacking transition-metal dopants did not show ferromagnetism under any conditions.

The data in Fig. 3 are particularly intriguing because they demonstrate post-synthetic manipulation of 300 K ferromagnetism in both $\text{Mn}^{2+}:\text{ZnO}$ and $\text{Co}^{2+}:\text{ZnO}$. To date, relatively few analogous chemical perturbations of DMS ferromagnetism have been demonstrated, all involving n -type defects [7,25]. Although uncertainties still surround some of these, such perturbations could become important mechanistic tools for testing and refining theoretical models. In the present case, all of the responses of $\text{Mn}^{2+}:\text{ZnO}$ and $\text{Co}^{2+}:\text{ZnO}$ to n - and p -type perturbations shown in Fig. 3 are consistent with theoretical predictions of hole-mediated ferromagnetism in $\text{Mn}^{2+}:\text{ZnO}$ and electron-mediated ferromagnetism in $\text{Co}^{2+}:\text{ZnO}$ [3–6]. For $\text{Mn}^{2+}:\text{ZnO}$, these calculations have predicted that the five $3d$ electrons of Mn^{2+} should be highly localized in the absence of p -type dopants. Indeed, the $\text{Mn}^{2+}:\text{ZnO}$ described here (Ref. [15] and see [16]) and stoichiometric $\text{Mn}^{2+}:\text{ZnO}$ described elsewhere [8] do show $S = 5/2$ Curie-Weiss paramagnetism in the absence of added nitrogen. At sufficiently high N concentrations, however, one of the Mn^{2+} t_2 electrons is predicted [3–5] to delocalize partially into the impurity band formed by the N shallow acceptors, stabilizing ferromagnetic ordering via a mechanism described as either Zener type [3] or double exchange [4]. These calculations also predict that carriers in n -type $\text{Mn}^{2+}:\text{ZnO}$ will not delocalize sufficiently onto the Mn^{2+} due to its large exchange energy but will instead remain in the conduction band or donor levels, prohibiting long-range $\text{Mn}^{2+}-\text{Mn}^{2+}$ ferromagnetic coupling mediated by itinerant electrons [4]. The demonstration here of predictable and controllable 300 K magnetic ordering in $\text{Mn}^{2+}:\text{ZnO}$ and $\text{Co}^{2+}:\text{ZnO}$ in response to targeted p -type (N) and n -type (Zn_i) perturbations provides experimental support for the general trends predicted by these theoretical models and represents an important advance toward the goal of elucidating the microscopic mechanisms behind intrinsic high- T_C ferromagnetism in ZnO DMSs.

Despite the clear phenomenological conclusions derived from the data in Figs. 1–3, several important questions remain. One unresolved issue is the chemical identity of the nitrogen, tentatively proposed to be N_O by analogy to other N-doped ZnO studies [1]. Binding nitrogen to Zn^{2+} at the colloid surfaces prior to calcination may greatly facilitate its incorporation into the lattice during sintering. A related question is whether an analogous post-synthetic p -type perturbation could successfully activate ferromag-

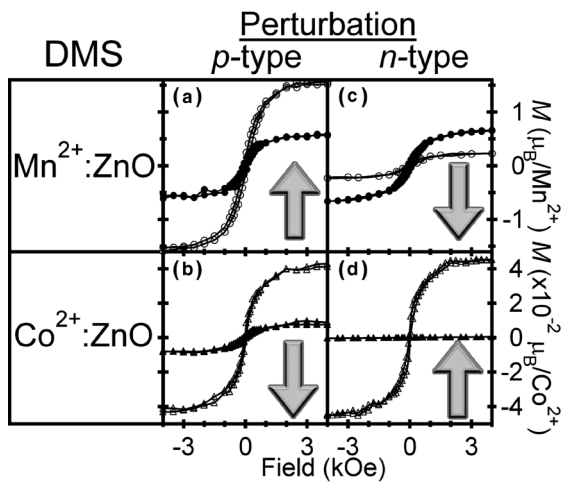


FIG. 3. 300 K magnetization vs field loops for 0.20% $\text{Mn}^{2+}:\text{ZnO}$ and 3.5% $\text{Co}^{2+}:\text{ZnO}$ films before and after various n - or p -type perturbations. Arrows indicate the increase (up) or decrease (down) of 300 K ferromagnetism upon perturbation. See text for details.

netism in epitaxial (low-surface-area) $\text{Mn}^{2+}:\text{ZnO}$. The successful *ex situ* activation of *p*-type conductivity in epitaxial ZnO films using NH_4NO_3 [22] is encouraging in this regard. A third outstanding question pertains to the relationship between T_C and defect concentration that would be anticipated from many models [3,6]. Experiments to address these important questions are under way.

In summary, we have demonstrated unprecedented chemical manipulation of high- T_C ferromagnetism in ZnO DMSs. The experimental results show a strong and unambiguous correlation between *p*-type perturbations and ferromagnetism in $\text{Mn}^{2+}:\text{ZnO}$ and a correspondingly clear inverse correlation in $\text{Co}^{2+}:\text{ZnO}$. Similarly clear but opposite trends were also observed for *n*-type perturbation by Zn vapor. These data are consistent with theoretical models in which ZnO DMS ferromagnetism is mediated by charge carriers [3–6]. More generally, these results suggest that it may eventually be possible to use *ex situ* chemical, electrochemical, or photochemical perturbations for real-time gating of high- T_C magnetic ordering in diluted magnetic oxides. Although these results are encouraging from a fundamental perspective, potential device applications will likely demand even greater coercivities and saturation moments as well as continued progress in understanding the electronic structures of the observed ferromagnetic phases.

This work was funded by the NSF (Grants No. DMR-0239325 and No. ECS-0224138). The authors are grateful to the UW/PNNL Joint Institute for Nanoscience (K.R.K.), the NSF-IGERT (N.S.N.), and the Cottrell Scholar program of the Research Corporation (D.R.G.).

-
- [1] D. C. Look and B. Claffin, *Phys. Status Solidi B* **241**, 624 (2004).
- [2] For a compilation of recent reviews, see *MRS Bull.*, edited by S. A. Chambers and Y. K. Yoo, Vol. 23, 706 (2003).
- [3] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, *Science* **287**, 1019 (2000).
- [4] K. Sato and H. Katayama-Yoshida, *Physica E (Amsterdam)* **10**, 251 (2001).
- [5] Q. Wang, Q. Sun, P. Jena, and Y. Kawazoe, *Phys. Rev. B* **70**, 052408 (2004).
- [6] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, *Phys. Rev. Lett.* **93**, 177206 (2004).
- [7] D. A. Schwartz and D. R. Gamelin, *Adv. Mater.* **16**, 2115 (2004).
- [8] X. Gratens, V. Bindilatti, N. F. Oliveira, Jr., Y. Shapira, S. Foner, Z. Golacki, and T. E. Haas, *Phys. Rev. B* **69**, 125209 (2004); S.-J. Han, T.-H. Jang, Y. B. Kim, B.-G. Park, J.-H. Park, and Y. H. Jeong, *Appl. Phys. Lett.* **83**, 920 (2003); S. W. Yoon, S.-B. Cho, S. C. We, S. Yoon, B. J. Suh, H. K. Song, and Y. J. Shin, *J. Appl. Phys.* **93**, 7879 (2003).
- [9] K. Ip, R. M. Frazier, Y. W. Heo, D. P. Norton, C. R. Abernathy, S. J. Pearton, J. Kelly, R. Rairigh, A. F. Hebard, J. M. Zavada, and R. G. Wilson, *J. Vac. Sci. Technol. B* **21**, 1476 (2003); S. W. Jung, S.-J. An, G.-C. Yi, C. U. Jung, S.-I. Lee, and S. Cho, *Appl. Phys. Lett.* **80**, 4561 (2002).
- [10] P. Sharma, A. Gupta, K. V. Rao, F. J. Owens, R. Sharma, R. Ahuja, J. M. Osorio Guillen, B. Johansson, and G. A. Gehring, *Nat. Mater.* **2**, 673 (2003).
- [11] S.-W. Lim, M.-C. Jeong, M.-H. Ham, and J.-M. Myoung, *Jpn. J. Appl. Phys.* **43**, L280 (2004).
- [12] Y. W. Heo, M. P. Ivill, K. Ip, D. P. Norton, S. J. Pearton, J. G. Kelly, R. Rairigh, A. F. Hebard, and T. Steiner, *Appl. Phys. Lett.* **84**, 2292 (2004).
- [13] D. C. Kundaliya, S. B. Ogale, S. E. Lofland, S. Dhar, C. J. Metting, S. R. Shinde, Z. Ma, B. Varughese, K. V. Ramanujachary, L. Salamanca-Riba, and T. Venkatesan, *Nat. Mater.* **3**, 709 (2004).
- [14] R. K. Zheng, H. Liu, X. X. Zhang, V. A. L. Roy, and A. B. Djuricic, *Appl. Phys. Lett.* **85**, 2589 (2004).
- [15] N. S. Norberg, K. R. Kittilstved, J. E. Amonette, R. K. Kukkadapu, D. A. Schwartz, and D. R. Gamelin, *J. Am. Chem. Soc.* **126**, 9387 (2004).
- [16] See EPAPS Document No. E-PRLTAO-94-018515 for supplementary material consisting of figures showing additional magnetic, x-ray diffraction, SEM, and TEM data. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory [/epaps/](ftp://ftp.aip.org/pub/epaps/). See the EPAPS homepage for more information.
- [17] C. H. Bates, W. B. White, and R. Roy, *J. Inorg. Nucl. Chem.* **28**, 397 (1966).
- [18] D. A. Schwartz, N. S. Norberg, Q. P. Nguyen, J. M. Parker, and D. R. Gamelin, *J. Am. Chem. Soc.* **125**, 13205 (2003).
- [19] J. H. Park, M. G. Kim, H. M. Jang, S. Ryu, and Y. M. Kim, *Appl. Phys. Lett.* **84**, 1338 (2004).
- [20] A. van Dijken, E. A. Meulenkaamp, D. Vanmaekelbergh, and A. Meijerink, *J. Phys. Chem. B* **104**, 1715 (2000); H. Zhou, H. Alves, D. M. Hofmann, W. Kriegseis, B. K. Meyer, G. Kaczmarczyk, and A. Hoffmann, *Appl. Phys. Lett.* **80**, 210 (2002).
- [21] C. G. Van de Walle and J. Neugebauer, *Nature (London)* **423**, 626 (2003); C. H. Seager and S. M. Myers, *J. Appl. Phys.* **94**, 2888 (2003).
- [22] J. F. Rommeluère, L. Svob, F. Jomard, J. Mimila-Arroyo, A. Lusson, V. Sallet, and Y. Marfaing, *Appl. Phys. Lett.* **83**, 287 (2003).
- [23] Z. Ji, C. Yang, K. Liu, and Z. Ye, *J. Cryst. Growth* **253**, 239 (2003).
- [24] D. G. Thomas, *J. Phys. Chem. Solids* **3**, 229 (1957).
- [25] T. Story, R. R. Galazka, R. B. Frankel, and P. A. Wolff, *Phys. Rev. Lett.* **56**, 777 (1986); S. T. B. Goennenwein, T. A. Wassner, H. Huebl, S. M. Brandt, J. B. Philipp, M. Opel, R. Gross, A. Koeder, W. Schoch, and A. Waag, *Phys. Rev. Lett.* **92**, 227202 (2004); A. Manivannan, G. Glaspell, and M. S. Seehra, *J. Appl. Phys.* **94**, 6994 (2003).