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Two state coercivity driven by phase coexistence in vanadium sesquioxide/nickel bulk hybrid material

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We developed a bulk hybrid material consisting of a vanadium sesquioxide (V2O3) matrix with nickel (Ni) rich inclusions that exhibit a switchable two-state magnetic coercivity. The V2O3 matrix magnetoelastically couples with the Ni-rich inclusions and its structural phase transition causes two possible magnetic coercivity states. Differences of up to 13% in the temperature window of 14 K are observed, depending whether the transition occurs from rhombohedral to monoclinic or vice versa. These findings provide a pathway for the development of bulk switchable coercivity materials. We present routes to further enhance the magnetoelastic effect by increasing the oxide/ferromagnetic material coupling. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4962155]

Magnetic hybrid materials are important for applications requiring controllable magnetic properties. This control has been demonstrated using external driving forces such as light,1,2 electric fields,3,4 current injection,5 and strain.6,7 In particular, strain affects the magnetization through the inverse magnetostriction effect.8–13 and in thin films, magnetic hybrids have been generated using piezoelectric, ferroelectric, and structural phase transitioning (SPT) multilayers or substrates.6,14–17 Nevertheless these studies on strain coupled hybrid materials have been done in thin films18,19 and not in bulk.

In this work, we present a bulk material, a vanadium sesquioxide (V2O3)/nickel hybrid, where the magnetic properties show a strong deviation from typical nickel temperature dependence and a two state coercivity. The unusual magnetic behavior of this hybrid is driven by the V2O3/SPT from monoclinic to rhombohedral phase.20,21 The center of the STP occurs at 150 K, but it is hysteretic and includes a region of phase coexistence.20,22,23 The SPT coincides with a metal to insulator (MIT) and paramagnet to antiferromagnet transition.23 Previous work on thin-film V2O3/ferromagnetic heterostructures showed that interfacial strain coupling between the ferromagnetic material (Ni, Fe, and Co) and the vanadium oxide leads to additional strain anisotropies due to the inverse magnetostriction effect.24 In these films, the coercivity change is characterized by two factors. First, the change between the low and high temperature phases due to inverse magnetostriiction, which typically corresponds to a two-fold coercivity change. Second, the coercivity enhancement during phase coexistence is caused by additional domain pinning in grain boundaries, which can lead to a three-fold coercivity change. This coercivity enhancement due to phase separation is strongly dependent on the interface quality, with rough films showing no enhancement.24,25

Here, we report that the interfacial strain also plays a key role in bulk Ni-V2O3 hybrids. We observe a fully reversible hysteresis between the coercivity states and unusual remnant magnetization behavior driven by the SPT of the oxide. By comparing different preparation procedures, we present a pathway for efficient interfacial strain coupling in bulk hybrid materials. This proof-of-concept opens up a variety of material combinations for bulk hybrids with tunable magnetic states.

The V2O3/Ni hybrid was fabricated from commercially obtained V2O3 (Sigma Aldrich 99.7%) and NiO (Sigma Aldrich, 99.8%) with a nominal mesh size of 63 μm. A mix consisting of V2O3 powder with 10% or 25% NiO powder was used. The two powders were combined using a sequence of three ball millings: 1.5 h with 1 mm diameter balls, 1 h with 0.5 mm balls, and 30 min with 0.2 mm balls. This decreased the average particle size to 0.68 μm. Following the milling process, 0.2 g from the ground powder mixture was compacted into 1 mm thick and 5 mm diameter pellets using two pressure conditions: 100 MPa and 200 MPa. In the last step, the pellets were sintered for 2 h under a hydrogen-nitrogen atmosphere (10% H2 and 90% N2) at temperatures between 500 °C and 1000 °C. This step selectively reduces the NiO to Ni and further improves the coupling between Ni and V2O3 due to an annealing effect to produce the hybrid material. In total, nine different bulk samples have been prepared and characterized.

Temperature dependent electrical transport was measured in a four probe configuration in an exchange gas cryostat between 80 K and 300 K in a temperature sweep mode at a constant current of 1 μA. Structural characterization using X-ray diffraction (XRD, λCuKα = 1.54 Å) was carried out simultaneously with an additional electrical transport measurement in the same temperature range with 2 K steps. Comparing the electrical transport results between the two measurements, it was found that the X-ray measurement nominal temperature had an 18 K lag.
energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) at room temperature. Magnetization as a function of field and temperature was recorded using a PPMS-DynaCool Vibrating Sample Magnetometer (VSM) in the temperature range between 10 K and 300 K.

XRD of the sintered samples at room temperature show only V$_2$O$_3$ and Ni diffraction peaks (Fig. 1). No other vanadium oxide phases or NiO were identified, indicating that the hydrogen-heat treatment reduces the NiO, while not significantly affecting the V$_2$O$_3$ stoichiometry. EDX measurements in combination with SEM indicate that the distribution of Ni within the pellet is spatially inhomogeneous and varies with the sintering temperatures. Ni-rich inclusions were found with a diameter of 1–2 μm that are distributed throughout the pellet (Fig. 2). Away from the inclusions, the V$_2$O$_3$ matrix appears porous with an average grain size of 100–300 nm for all sintering temperatures. In contrast, the morphology of the Ni-rich inclusions changes with sintering temperature. At the sintering temperature of 700°C (Fig. 2(a)) the morphology of the inclusions is similar to that of the matrix, however at 900°C (Fig. 2(b)) the surface of the inclusion appears to become smoother. Finally at 1000°C (Fig. 2(c)), the inclusions appear as dense 1 μm metallic droplets. For the starting powder composition of 10% NiO by weight, which translates to an elemental Ni concentration of 7.9% after the sintering process, the EDX reveals a Ni concentration of 35% in the inclusions and 7% Ni in the neighboring matrix. This special concentration difference is independent of the applied pressure and the sintering temperature. However, the scattering volume of the EDX is about 30 μm$^3$, which causes averaging over the inclusions and the surrounding matrix and thus prevents a more quantitative analysis.

Transport measurements of all Ni-V$_2$O$_3$ pellets sintered above 500°C show a hysteretic MIT occurring between 120 K and 160 K with a resistance change of four orders of magnitude (see the supplementary material). This creates a two resistance state in a defined temperature range around the MIT. The transition temperature varies with sintering temperature. This is likely connected to a small variation in oxygen content due to the sintering and hydrogen treatment. As an example, we present in Fig. 3 the results of a sample prepared with 25% NiO, ball milled, pressurized at 200 MPa, and sintered at 900°C. We found that the transition occurs at 142 K (center of the hysteretic curves in Fig. 3(a)) over a temperature window of 40 K and it shows the expected thermal hysteresis of a first-order phase transition (Fig. 3(a)).

Fig. 3(b) illustrates the effect of the V$_2$O$_3$ SPT by comparing selected XRD peaks well above (200 K) and below (100 K) the phase transition. The intensity at each temperature has been fitted with two Gaussian functions whose integrated areas reflect the phase evolution (Fig. 3(c)). During the transition, the integrated area of the monoclinic (011)–V$_2$O$_3$ peak at 2θ = 24.2° decreases with increasing temperature, while the (012) peak area of rhombohedral V$_2$O$_3$ at an angle of 2θ = 24.3° increases. A similar analysis was performed for the monoclinic (002) at 2θ = 32.5° and (211) at θ = 33.2°, which merge to the high-temperature rhombohedral (104) peak at 2θ = 33.0°. The individual intensities are normalized and compared as a function of temperature (Figure 3(c)). The crossing of the intensities at 50% is taken as the SPT transition temperature, which after thermometry correction is $T_{XRD} = 145$ K.

The pellet magnetization as a function of field and temperature is shown in Fig. 4. Taking into account the Ni mass of each sample from the NiO concentration in the initial mixture, the saturation magnetization as a function of temperature, $M_s(T)$ measured in 6 kOe, is within 6% of the literature value for pure Ni powder. This supports the XRD results of a nearly complete conversion of NiO to Ni for all sintering temperatures.

Outside the SPT region of V$_2$O$_3$, the coercivity of all samples increases approximately linearly from 300 K to 10 K with values much larger than found in Ni powder. While all samples show this temperature dependence of the coercivity,
only the samples produced by ball milling and sintered at 900 °C show a unique two state coercivity behavior (Figs. 4(b) and 4(c)). At one fixed temperature, the two states differ by up to 13% (160 Oe in the low coercivity state and 180 Oe in the high coercivity state) for a temperature window of 14 K between 138 K and 152 K (Fig. 4(b)). Furthermore, the remanent magnetization of the hybrid after saturation at 6 kOe exhibits an atypical behavior when compared to pure Ni or pure V2O3 with a prominent change in slope occurring at the V2O3 SPT temperature (Fig. 4(d)). The change in coercivity of samples compressed with 100 MPa or 200 MPa or with different initial NiO content, 10% or 25%, is negligible. A more detailed view of the magnetization results for other preparation conditions can be found in the supplementary material. All observations of changes to the magnetic properties as a function of temperature, i.e., coercivity and magnetization, were fully reversible within subsequent cycles and fully reproducible over a period of two years including several tens of temperature cycles.

The hysteresis in coercivity and the atypical remnant magnetization indicate a connection of the hybrid’s magnetic properties to the SPT of V2O3. Similar effects were observed in hybrid thin films of V2O3 combined with Ni, Fe, or Co. The change in coercivity and magnetization was interpreted as due to interfacial strain coupling in which the SPT of V2O3 induces additional anisotropies in the Ni film. The observations were limited to thin films and therefore well-defined interfaces between the materials.

To estimate the expected coercivity change, we use a strain coupling model by Klemens for composite materials with different thermal expansion coefficients (see the supplementary material). Considering a V2O3 volume increase of 1.5% and resulting effective thermal expansion coefficient of ~10^{-4} K^{-1}, the stress acting on the Ni particles (thermal expansion coefficient of 1.3 × 10^{-5} K^{-1}) is estimated to be 290 MPa (see the supplementary material). Based on this strain and the associated stress anisotropy field, the change in coercivity can be estimated to 600 Oe, which is consistent with large coercivity enhancement observed in thin films. The observed experimental value of 20 Oe reported here is more than an order of magnitude below this estimate. This is due to two effects. First, porosity in V2O3 matrices (Fig. 2) causes strain relief, which diminishes the effective stress on the Ni-rich inclusions. Second, the Ni-rich inclusions themselves have grain boundaries, which can cause additional strain relaxation. This leaves room for future work which could decrease sources of stress relaxation potentially increasing the difference between the two coercivity states to 300% which is observed in thin film bilayers. This can be potentially achieved by fine tuning the synthesis conditions like the sintering temperature, the H concentration, the cooling rate, the ferromagnetic metal concentration, or by using Ni instead of NiO which creates a pore separation due to the reduction process. Also, more grinding and compacting cycles of the sintered pellets with additional sintering cycles will likely lead to an improved interface between the Ni in the V2O3 matrix. More elaborate preparation procedures could envisage direct coating of V2O3 nanoparticles with a ferromagnetic metal or the use of ferromagnetic oxides, which provide a stronger coupling with the oxide host. This could allow thin-film level smoothness at the interface, which is critical for a large coercivity enhancement. Another alternative approach would be to use materials with larger magnetostriction than Ni.

FIG. 4. Magnetic characterization of a pellet with 25% initial NiO, ball milled, 200 MPa applied pressure, and sintered at 900 °C. (a) Magnetization as a function of applied magnetic field. Three example hysteresis loops at different temperatures show the coercivity change of the magnetic Ni. (b) Coercivity extracted from hysteresis loops as a function of temperature. Two coercivity states at the same temperature are marked as state 1 and state 2 by the two open circles. (c) Heating branch of the magnetization in remanence as a function of temperature: A clear change in slope is visible at 160 K compared to the pure Ni sample or a V2O3 pellet.
(Gerfenol and Terfenol) or host materials with a larger volume change during the transition would also increase the coercivity change.

In summary, we developed a bulk hybrid material consisting of vanadium sesquioxide and nickel which exhibits a two state coercivity in a 14 K temperature window next to a two state resistance in the same temperature window. While the change between the low and high coercivity states is only 13%, it can be potentially enhanced by more than one order of magnitude by improving the magnetoelastic coupling between Ni-rich inclusions and the V$_2$O$_3$ matrix. The two state coercivity concurrent with the change in resistance in bulk material can be leveraged in the development of power electronics and magnetic devices. Finally, our work highlights the importance of the intrinsic morphology of hybrid materials and provides pathways for exploring other oxides with a hysteretic STP that can couple to magnetic properties of ferromagnets generating two state magnetic and electronic systems.

See supplementary material for more detailed information about the electrical transport measurements, the remanence properties of the hybrid pellet samples and the strain model used.

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