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Millisecond direct measurement of the magnetocaloric effect of a Fe_2P-based compound by the mirage effect

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We present direct measurements of the magnetocaloric effect on a Fe_2P-based compound induced by a milliseconds pulsed magnetic field of 1 T to test their possible use in high frequency (up to 100 Hz) thermomagnetic cycles. The reported measurements were performed with an innovative and versatile non-contact set up based on the mirage effect. The adiabatic temperature change of a $MnFeP_{0.45}As_{0.55}$ sample is presented and compared with measurements performed varying the same magnetic field in a time interval of 1 s and 100 ms. These results demonstrate the absence of kinetic constraints in the first-order phase transition of this sample induced on the milliseconds time scale. The study of the materials' response to millisecond magnetic field pulses represents a fundamental test for the development of more powerful and efficient magnetic refrigerators. [http://dx.doi.org/10.1063/1.4939451]

Magnetocaloric room-temperature devices are a generation of refrigerators aiming at a more efficient production of cooling power.[1–3] The recent discovery of a class of inexpensive compounds[4–6] based on Fe_2P, showing high and reversible changes of temperature (ΔT_{ad}) and entropy (ΔS_T) in magnetic field ranges ($\Delta B = 1$ T) that are reasonable for real machines, is now pushing the envelope.[7]

The excellent magnetocaloric performance of these materials derives from a first-order isosymmetric magneto-elastic phase transition.[8–10] This phase transition is highly composition sensitive,[4] acting as a handle to tune adiabatic temperature and entropy changes, thermal and field hysteresis as well as to improve mechanical stability. Only recently, the physical origin of the first-order phase transition in Fe_2P-based materials has become clear. Predicted by *ab initio* calculations and recently observed experimentally, mixed magnetism[11] is a direct consequence of the transition metal main group element bond nature in Fe_2P-based materials. This phenomenon consists of an electronic density reconstruction occurring at T_C, which is responsible for the first-order phase transition itself.

Alongside the search for materials with improved magnetocaloric properties, magnetocaloric characterization is also evolving.[12] The development of magnetic refrigerators and energy conversion devices requires (1) reliable estimations of the material's reversible and irreversible thermo-magnetic properties, (2) to explore the materials magnetocaloric response on frequency ranges comparable with those envisioned for applications. In-field calorimetry and conventional direct temperature change probes tackle the first task.[13–18] On the other hand, the thermal capacity of the temperature sensor itself hinders the use of these setups for high frequency measurements. In this context, non-contact temperature change setups are useful solutions to rule out, or at least reduce, the thermal capacity of the temperature sensor.[19–21] This feature both enhances the measurement accuracy and reduces the time constant of temperature change measurement.[18,19,22] These experimental setups are also promising solutions to directly measure the magnetocaloric effect (MCE) of systems with low dimensionality, such as free-standing thin films and ribbons.[23]

In this work, we explore the magnetocaloric time response of a $MnFeP_{0.45}As_{0.55}$ sample across its first-order magneto-elastic transition. This compound shows ideal magnetocaloric properties and it is the precursor of the modern Si-substituted Fe_2P-based material family,[8,24] which comprises the most promising materials for applications developed to date. The direct measurement of the magnetocaloric effect on different time scales is fundamental to probe the time constant of the magnetic transition aimed at verifying the usefulness of materials as active elements in thermomagnetic cycles at different frequencies.[25] In this work we aim at ultimately testing the suitability of Fe_2P-based compounds for applications that require high frequency cycling.

For this purpose, we have developed a non-contact technique, based on the mirage effect suitable to probe the dynamic response of magnetic phase transitions. The realized setup is capable of direct measurements of the magnetocaloric effect in bulk samples triggered by fast magnetic field pulses with an amplitude up to 1 T and a rise time of the

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order of 1 ms. This setup thus simulates the operating conditions of a hypothetical machine performing thermomagnetic cycles at 100 Hz (Ref. 25) with a magnetic field up to 1 T.

This non-contact technique is based on an optical beam deflection method already used to measure the thermal diffusivity and the thermo-optical absorption spectrum of materials (photothermal spectroscopy).[26–28] In the latter techniques, the material's temperature change, induced by optical absorption or resistance heating, produces a time varying gradient of the refractive index in the surrounding medium (air), which can be detected by the deflection of a probe laser beam travelling through the air layer immediately adjacent to the sample surface (Mirage Effect). In the studied case, the material's temperature change is due to the MCE driven by the magnetic field pulse. We show, in this work, that the thermal diffusion time to the gas layer next to the sample surface is fast enough to probe the material's magnetocaloric response to short pulses of the order of milliseconds. The reliability of this method is confirmed by comparing our results with those obtained using a different technique.

The investigated sample was prepared by ball milling and subsequent annealing of high purity elements in adequate proportions. A sample of approximately 4 g was loaded in the crucible of a SPEX-8000 mill with four 6.35 mm diameter stainless steel balls and milled for 1 h under Ar atmosphere. The milling resulted in a very fine powder, which was pressed into pellets of 3 mm diameter and 3 to 5 mm thickness under a force of about 5 kN. The pellets were then sealed in quartz ampoules under Ar atmosphere and annealed at 1273 K for 100 h then at 923 K for 120 h using a heating/cooling rate of 1 K min^{-1}. X-ray powder diffraction measurements, performed at room temperature using Cu Kα radiation ($\lambda = 0.15418$ nm), show that the material crystallises in the Fe_2P-type structure (space group P-62 m). The lattice parameters obtained from Rietveld refinement are a = 6.1659(5) Å and c = 3.463(2) Å resulting in a c/a ratio of 0.5616.

Isofield magnetic measurements have been performed using a Quantum Design Inc. MPMS 5XL SQUID magnetometer across the magnetic transition with temperature sweeps in heating and cooling at a rate of 1 K/min (see Figure 1). The narrow thermal hysteresis (1.8 K) and the strong dependence of the transition temperature on the magnetic field (dT/dB = 5.3 K/T) are in agreement with previous reports.[8,24] The isothermal entropy change (ΔS) was calculated using the Maxwell relations. Previous works demonstrated their suitability also in the case of first-order phase transitions if the proper measurement protocol is followed.[16–29] The entropy change exhibits a peak of 8.9 ± 0.3 J kg^{-1} K^{-1} at 305.5 K for a 1 T magnetic field change (see inset of Figure 1). The heating and cooling $\Delta S(T)$ curves overlap across their peak value showing the complete reversibility of the MCE in this compound for this magnetic field span. This has been confirmed by measuring the adiabatic temperature change (ΔT_{ad}) of subsequent thermomagnetic cycles where no differences between the first and the following branches were observed.

The experimental setup for the dynamic MCE response measurement is displayed schematically in Figure 2. It

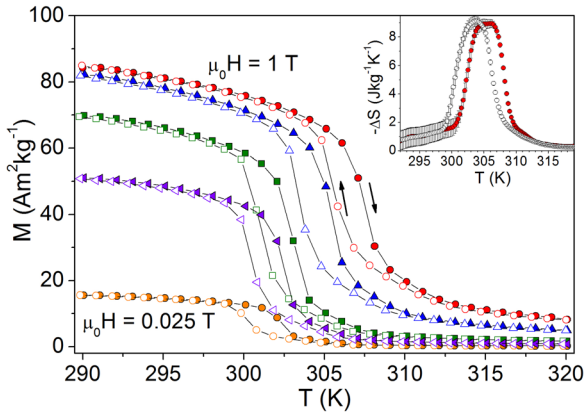

FIG. 1. Isofield measurements of $MnFeP_{0.45}As_{0.55}$ at μ_0H = 0.025 T, 0.1 T, 0.2 T, 0.6 T, 1 T, in heating (filled symbols) and in cooling (empty symbols). Inset: isothermal entropy variation for a magnetic field change of 1 T in heating (red circles) and in cooling (white circles).

consists of a laser, a sample holder, a coil, and a detector. The probe beam is a red ($\lambda = 632.8$ nm) helium-neon laser, characterized by a long-term amplitude stability and low noise. The sample is glued with an insulating varnish onto a sample holder, whose temperature can be controlled and stabilized by a resistive heater and a Pt100 temperature sensor. The sample holder is inserted inside a small coil (external diameter 3 cm) and mounted onto a micro-positioning device, which allows accurate alignment of the sample surface parallel to the laser beam. The magnetic field is generated by the controlled discharge of a capacitors bank. Different magnetic field pulses of maximum amplitude $\mu_0 H = 1$ T and a rise time between 1 and 3 ms can be generated by varying the capacitance and the geometry of the coil. The spatial homogeneity of the field was measured with a Lakeshore 460 Hall probe gaussmeter: within the coil, a region of about 1 cm along the coil axis shows a field homogeneity better than

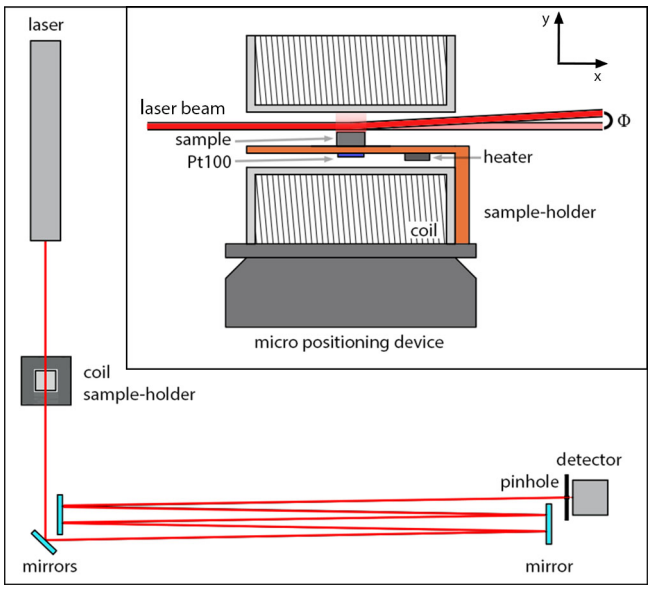

FIG. 2. Sketch of the developed setup for direct ΔT_{ad} measurements with pulsed magnetic fields. On the top: details of the sample holder inserted onto the coil and mounted above a micro positioning device. The magnetic pulsed field generates a temperature variation of the sample that deflects the laser beam, aligned close to its surface, of an angle Φ.

10%. A single element silicon photoconductive detector picks up the deflection of the laser beam. In front of the sensor, a pinhole (0.5 mm diameter) is used to select only a small portion of the laser beam profile. A Hall probe tracks the magnetic field pulse and triggers the acquisition of the photodetector. The output signal of the detector is acquired and amplified by an oscilloscope. Between sample and detector, two mirrors extend the optical path of the laser beam as to amplify the resultant deflection at the detector position.

From geometric optics theory of photothermal spectroscopy, the deflection angle of the probe beam (Φ) in one dimension can be written as[30]

$$\Phi(y,t) = \frac{1}{n}\frac{dn}{dT}\frac{\partial T(y,t)}{\partial y}d, \quad (1)$$

where n is the refractive index of the deflecting medium, dn/dT is the temperature coefficient of the refractive index, and d is the length of the laser path across the temperature gradient (in our case d is the sample length since each part of the sample experiences the same temperature change). For small temperature variations, dn/dT can be considered constant, while the temperature gradient ($\partial T/\partial y$) is a function of the temperature of the sample. The deflection angle (Φ), and thus the change of intensity (ΔI) at the detector position, therefore depends on the temperature and on the length of the sample.

When Φ is small, ΔI is directly proportional to Φ since a small portion of the Gaussian profile of the laser beam section at the detector position can be approximated as linear. This allows us to assume that the measured laser intensity change (ΔV) is proportional to the temperature variation of the sample (ΔT). This proportionality has been verified by measuring the ΔT_{ad} of a Gadolinium sample across its Curie temperature as a function of the amplitude of the magnetic field pulses. The achieved results are comparable with those obtained from a previously described setup based on a Cernox temperature sensor.[18] This comparison also allowed us to deduce the proportionality coefficient. Through this calibration, the absolute temperature change of the sample, induced by the magnetic field pulse, can be derived from the measured variation of the detector output (ΔV), provided that the different measurements are carried out with the same geometrical configuration of the experimental setup (positions of laser beam, sample, and detector).

The small measurement time constant is the key feature of this experimental setup. It is ruled mainly by the heat transfer through the medium in contact with the sample surface. The characteristic time for heat exchange between the sample surface and a point at a distance h in the deflecting medium is $\tau \approx h^2/4\alpha$, where α is the thermal diffusivity of the medium.[31] Considering that the present technique operates in air ($\alpha = 1.9 \times 10^{-5}\,m^2/s$) and that the laser beam is positioned within $h = 0.1$ mm above the sample surface, the resulting characteristic time constant of this setup can be calculated as $\tau \approx h^2/4\alpha \approx 0.5$ ms. Simulations of heat transfer and experimental tests carried out positioning the laser beam farther away from the sample surface confirm that the time constant (τ) is of the order of tenths of ms, making this experimental setup suitable to study the material's response at frequencies of hundreds of Hertz. In these experimental conditions, we also estimated that the Joule heating induced by eddy currents in a Gd sample is less than 0.1 K.

In the following, we show the results of a series of measurements performed on the $MnFeP_{0.45}As_{0.55}$ sample. The specimen was cut in the shape of a $2.1 \times 4.4 \times 2.9\,mm^3$ parallelepiped. We probed the sample response to a magnetic field pulse with peak value $\mu_0 \Delta H_{max} = 1$ T and rise time 1.3 ms. In Figure 3 the output of the photodiode for a single measurement and the signal of the magnetic field pulse are normalized, superimposed, and plotted as a function of time. A delay of about 0.3 ms is found between the detected signal and the magnetic field pulse profile, while the overall shapes of the two curves match well except for their "tails" on the right side. The delay between the detector signal and the magnetic field pulse corresponds to the characteristic time for heat exchange between the sample surface and the air layer to occur. This result highlights that, even in the fast dynamic regime of $MnFeP_{0.45}As_{0.55}$, the heat transfer between the material and the surroundings is slower than the material's response to the external field pulse, as previously observed for other systems at lower frequencies.[22,32] The faster decrease of temperature with respect to the reduction of the magnetic field is likely to be caused by the combination of the cooling due to the MCE and of the heat transfer to the sample holder.

We measured the response of the sample to the same magnetic field pulse at different starting temperatures between 290 K and 312 K (Figure 4). The peak value of the measured ΔT_{ad} is 2.3 ± 0.2 K at 301.2 K, comparable with values reported in Refs. 24 and 33. The detector noise is the main source of error and it induces an uncertainty on the measured ΔT_{ad} of about ± 0.2 K, while other sources of error (i.e., integration on the length of sample and proportionality between ΔI and Φ) are estimated to be negligible.

The results obtained with the presented technique (red triangles) are compared in Figure 4 with the measurements performed on the same $MnFeP_{0.45}As_{0.55}$ sample with the setup described in Ref. 18. These latter direct measurements have been carried out varying the magnetic field in two different ways: moving the sample inside a static magnetic field by means of a pneumatic piston (field sweep ≈ 100 ms—yellow circles) or turning on a low inductive electromagnet (field sweep ≈ 1 s—cyan squares). The three measurements, characterized by different rise times of the magnetic field, give consistent results.

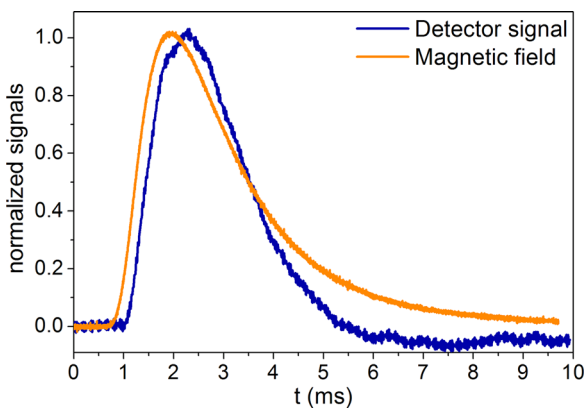

FIG. 3. Normalized variation of the photodiode signal (blue line) during the application of the magnetic field pulse (orange line) on $MnFeP_{0.45}As_{0.55}$ at 302 K.

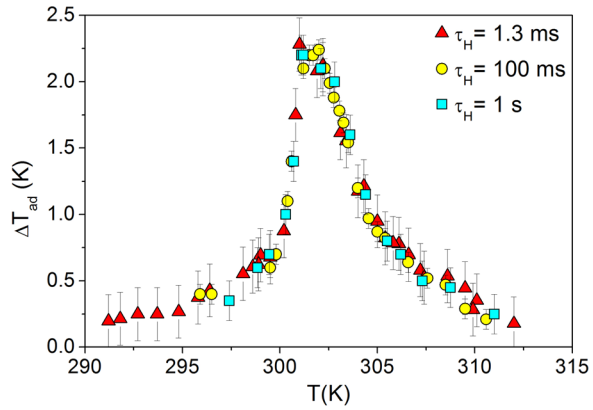

FIG. 4. $\Delta T_{ad}(T)$ of $MnFeP_{0.45}As_{0.55}$ directly measured with the presented setup (red triangles) and with a Cernox based probe[18] characterized by a rise time of the magnetic field of about 100 ms (yellow circles) or 1 s (cyan squares). In all measurements: $\mu_0\Delta H = 1$ T.

These measurements probe the magnetocaloric response of Fe_2P-based materials to fast magnetic field pulses simulating high frequency (hundreds of Hertz) operating conditions. On the one hand, this work shows that it is possible to measure the dynamic response of very fast first-order phase transitions using a non-contact technique. On the other hand, we observed that the response of this material is the same to different magnetic field pulse lengths (1 T/s, 10 T/s, 750 T/s). This means that the time for heat exchange within the material and from the material to the surroundings is longer than the intrinsic magnetocaloric response to the external field pulse. Thus, there is no lag in the response to the magnetic field due to the dynamics of the phase transition (i.e., magnetocaloric effect) itself, making these materials capable of operating at the frequencies required for efficient magnetic refrigeration.

In summary, we have developed an innovative non-contact temperature change measurement technique based on the mirage effect aiming at testing magnetocaloric materials' response to fast magnetic field pulses simulating high frequency operating conditions. We have shown that Fe_2P-based compounds not only present the best standard magnetocaloric properties found to date, but also outstanding dynamic response, making them ideal for applications. The measurement technique itself represents a breakthrough: the measurement time constant is reduced below one millisecond allowing the measurement of the material's response in extreme operating conditions (1 T at a frequency of about 150 Hz). The reported measurement technique is simple and versatile, the short measuring time ensures good adiabaticity, making it specially suitable for characterizing low dimensionality samples (free-standing films, foils, and ribbons), which represent a challenge using conventional techniques.

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[1]A. Kitanovski, J. Tušek, U. Tomc, U. Plaznik, M. Ozbolt, and A. Poredoš, *Magnetocaloric Energy Conversion* (Springer International Publishing, Switzerland, 2015).
[2]S. B. Roy, "Magnetocaloric effect in intermetallic compounds and alloys," in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 2014), Vol. 22, Chap. 2.
[3]A. Smith, C. R. H. Bahl, R. Bjørk, K. Engelbrecht, K. K. Nielsen, and N. Pryds, Adv. Energy Mater. **2**, 1288 (2012).
[4]F. Guillou, G. Porcari, H. Yibole, N. van Dijk, and E. Brück, Adv. Mater. **26**, 2671 (2014).
[5]F. Guillou, H. Yibole, G. Porcari, L. Zhang, H. H. van Dijk, and E. Brück, J. Appl. Phys. **116**, 063903 (2014).
[6]F. Guillou, H. Yibole, N. H. van Dijk, L. Zhang, V. Hardy, and E. Brück, J. Alloys Compd. **617**, 569 (2014).
[7]See https://www.youtube.com/watch?v=Py9IaztpKzs for Informative video on magnetocaloric refrigeration.
[8]O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature **415**, 150 (2002).
[9]N. H. Dung, L. Zhang, Z. Q. Ou, and E. Brück, Appl. Phys. Lett. **99**, 092511 (2011).
[10]N. T. Trung, Z. Q. Ou, T. J. Gortenmulder, O. Tegus, K. H. J. Buschow, and E. Brück, Appl. Phys. Lett. **94**, 102513 (2009).
[11]N. H. Dung, Z. Q. Ou, L. Caron, L. Zhang, D. T. C. Thanh, G. A. de Wijs, R. A. de Groot, K. H. J. Buschow, and E. Brück, Adv. Energy Mater. **1**, 1215 (2011).
[12]K. G. Sandeman, *Magnetic Measurement Standardization* (Magnetics Technology International, 2014), pp. 72–78.
[13]J. Marcos, F. Casanova, X. Batlle, A. Labarta, A. Planes, and L. Mañosa, Rev. Sci. Instrum. **74**, 4768 (2003).
[14]S. Jeppesen, S. Linderoth, N. Pryds, L. T. Kuhn, and J. B. Jensen, Rev. Sci. Instrum. **79**, 083901 (2008).
[15]V. Basso, C. P. Sasso, K. P. Skokov, O. Gutfleisch, and V. V. Khovaylo, Phys. Rev. B **85**, 014430 (2012).
[16]G. Porcari, F. Cugini, S. Fabbrici, C. Pernechele, F. Albertini, M. Buzzi, M. Mangia, and M. Solzi, Phys. Rev. B **86**, 104432 (2012).
[17]K. Morrison, K. G. Sandeman, L. F. Cohen, C. P. Sasso, V. Basso, A. Barcza, M. Katter, J. D. Moore, K. P. Skokov, and O. Gutfleisch, Int. J. Refrig. **35**, 1528 (2012).
[18]G. Porcari, M. Buzzi, F. Cugini, R. Pellicelli, C. Pernechele, L. Caron, E. Brück, and M. Solzi, Rev. Sci. Instrum. **84**, 073907 (2013).
[19]F. Cugini, G. Porcari, and M. Solzi, Rev. Sci. Instrum. **85**, 074902 (2014).
[20]A. O. Guimaraes, M. E. Soffner, A. M. Mansanares, A. A. Coelho, A. Magnus, G. Carvalho, M. J. M. Pires, S. Gama, and E. C. da Silva, Phys. Rev. B **80**, 134406 (2009).
[21]J. Döntgen, J. Rudolph, T. Gottschall, O. Gutfleisch, S. Salomon, A. Ludwig, and D. Hägele, Appl. Phys. Lett. **106**, 032408 (2015).
[22]G. Porcari, K. Morrison, F. Cugini, J. Turcaud, F. Guillou, A. Berenov, N. H. van Dijk, E. H. Brück, L. F. Cohen, and M. Solzi, Int. J. Refrig. **59**, 29–36 (2015).
[23]C. W. Miller, D. D. Belyea, and B. J. Kirby, J. Vac. Sci. Technol., A **32**, 040802 (2014).
[24]H. Yibole, F. Guillou, L. Zhang, N. H. van Dijk, and E. Brück, J. Phys. D: Appl. Phys. **47**, 075002 (2014).
[25]M. D. Kuz'min, Appl. Phys. Lett. **90**, 251916 (2007).
[26]P. K. Kuo, M. J. Lin, C. B. Reyes, L. D. Favro, R. L. Thomas, D. S. Kim, S. Zhang, L. J. Inglehart, D. Fournier, A. C. Boccara, and N. Yacoubi, Can. J. Phys. **64**, 1165 (1986).
[27]A. C. Boccara, D. Fournier, and J. Badoz, Appl. Phys. Lett. **36**, 130 (1980).
[28]J. C. Murphy and L. C. Aamodt, J. Appl. Phys. **51**, 4580 (1980).
[29]L. Caron, Z. Q. Ou, T. T. Nguyen, D. T. C. Thanh, O. Tegus, and E. Brück, J. Magn. Magn. Mater. **321**, 3559–3566 (2009).
[30]J. Zhou, L. Zhao, J. Shen, and M. L. Baesso, J. Opt. Soc. Am. B **22**, 2409 (2005); J. D. Rudnicki and F. R. McLarnon, "In situ characterization of electrode processes by photothermal deflection spectroscopy," in *Techniques for Characterization of Electrodes and Electrochemical Processes*, edited by R. Varma and J. R. Selman (Wiley, 1991), pp. 127–166.
[31]J. Zhao, J. Shen, C. Hu, and J. Zhou, J. Opt. Soc. Am. B **21**, 1065 (2004).
[32]E. Lovell, A. M. Pereira, A. D. Caplin, J. Lyubina, and L. F. Cohen, Adv. Energy Mater. **5**, 1401639 (2015).
[33]K. Engelbrecht, K. K. Nielsen, C. R. H. Bahl, C. P. Carroll, and D. van Asten, J. Appl. Phys. **113**, 173510 (2013).