AIP Advances

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Cite as: AIP Advances **11**, 015312 (2021); https://doi.org/10.1063/9.0000102
Submitted: 14 October 2020 • Accepted: 25 November 2020 • Published Online: 06 January 2021

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Presented: 2 November 2020 • Submitted: 14 October 2020 •
Accepted: 25 November 2020 • Published Online: 6 January 2021

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Note: This paper was presented at the 65th Annual Conference on Magnetism and Magnetic Materials.
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ABSTRACT

In this work, we study the effect of elemental iodine as a halide intermediary in the synthesis of $FePt_3$ nanoparticles using a co-reduction of $Fe(acac)_3$ and $(NH_4)_2PtCl_2$ with 1,2-hexadecanediol. Our study shows that elemental iodine facilitates the formation of $FePt_3$ nanoparticles with the $L1_2$ structure. When iodine is not used, the as-made nanoparticles have mostly the disordered fcc $FePt_3$ structure. The as-made nanoparticles are ferromagnetic and have a Curie temperature close to 380 K. Annealing of the as-made nanoparticles leads to an increased particle size and a transformation to the ordered $L1_2$ $FePt_3$ phase. Nanoparticles annealed at 700°C for 30 minutes show a mixture of two magnetic phases, a ferromagnetic phase with a lower ordering temperature of ~300 K and an antiferromagnetic phase with a Néel temperature around 135 K.

I. INTRODUCTION

The structural and magnetic properties FePt nanoparticles are highly dependent on chemical composition, which can be tailored for potential applications in ultrahigh density storage media, biomedicine and catalysis.[1–5] Most of the studies so far have been focused on equiatomic Fe-Pt with the highly anisotropic $L1_0$ structure.[1–7] Recently, $L1_0$ FePt nanoparticles have been chemically synthesized through a halide mediated route without requiring any post annealing heat treatment.[8,9] Strong bonds between Fe^{3+} and Pt^{2+} ions and the halide ions facilitate the formation of FePt, through an energetically favorable way, thus leading to the formation of an ordered state.

In our experiments, we used elemental iodine to synthesize this phase, but our results showed that the $L1_2$ $FePt_3$ phase is obtained instead of the $L1_0$ phase. In bulk, $FePt_3$ with the $L1_2$ structure is known to be paramagnetic at room temperature and shows two coexisting antiferromagnetic transitions at T_{N1}~160 K and T_{N2}~120 K.[10] Previously, reported work on $FePt_3$ nanoparticles highlighted the antiferromagnetic to ferromagnetic transitions, which depend on the size and chemical ordering of the particles.[11–14] $FePt_3$ nanoparticles have also been shown to have an effective magnetic anisotropy energy density at least twice the value of the corresponding bulk values.[13]

In this work, we study the structural and magnetic properties of the $FePt_3$ nanoparticles made by using iodine. We also report the effect of annealing at different temperatures up to 700°C on the particle size, the structure and degree of ordering and the magnetic properties of the $FePt_3$ nanoparticles.

II. EXPERIMENTAL METHOD

The nanoparticles were chemically synthesized by the co-reduction of iron and platinum-based precursors in the presence of elemental iodine. In a typical reaction, which we will denote as the standard reaction, 0.25 mmol of iron(iii) acetylacetonate ($Fe(acac)_3$), 0.25 mmol of ammonium tetracholoroplatinate(ii) ($(NH_2)_2PtCl_2$) and 1 mmol of 1,2-hexadecanediol were mixed in a three-neck flask in a mixture of 18 ml trioctylamine (TO) and 2 ml oleylamine (OAm). The mixture

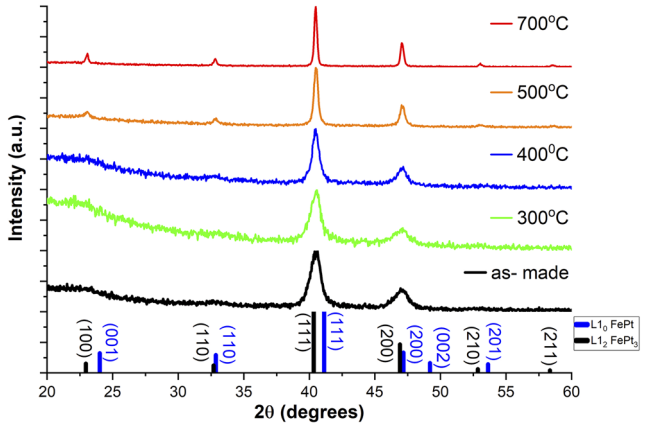

FIG. 1. X Ray diffraction patterns of as-made and annealed nanoparticles obtained from the standard reaction A. All annealing times were 30 minutes.

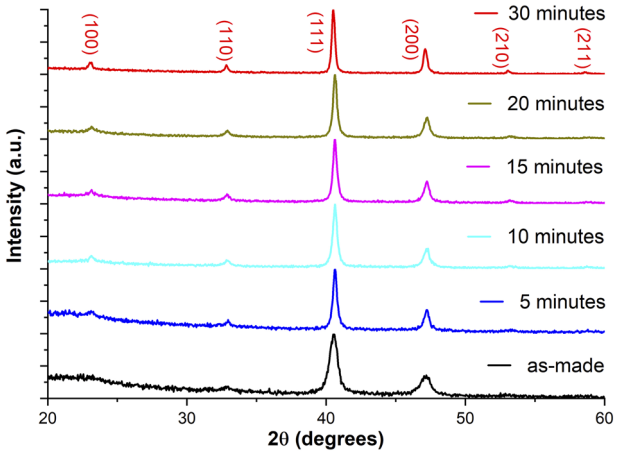

FIG. 3. X-ray diffraction patterns of as-made nanoparticles (made by a different reaction with 1:1 TO/OAm solvent ratio) and nanoparticles annealed at 700°C for different durations. Indexed peaks are those of $L1_2$ $FePt_3$.

was purged under forming gas (5% H_2 – 95% Ar) for 30 minutes in the temperature range of 60 – 80°C.

After 30 minutes, 250 mg of iodine was added to the mixture which was purged for an additional 30 minutes under forming gas. The mixture was then heated in order to obtain a reaction temperature in the range of 280°C – 300°C, which was at the threshold of boiling of the mixture. Afterwards, the solution was cooled to room temperature, and the resulting solution was washed with ethanol and hexane. The black resulting powder was isolated from the solution magnetically before being dried in a desiccator at room temperature. The as-made nanoparticles were annealed at different temperatures from 300-700°C and for different durations by sealing them in quartz tubes using a rough pump and diffusion vacuum pump filled with forming gas (5% H_2 - 95% Ar) before subjecting them to heat treatment.

The crystal structure of both the as-made and annealed nanoparticles was analyzed using X-ray diffraction (XRD), and their magnetic properties were measured using a vibrating sample magnetometer (Versalab VSM). The magnetic properties of some samples were also measured using a physical property measurement system (PPMS).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD data of the as-made sample and samples annealed at different temperatures made from the standard reaction. The as-made sample contains mainly the disordered fcc $FePt_3$ structure. However, some $L1_2$ $FePt_3$ is also present, as

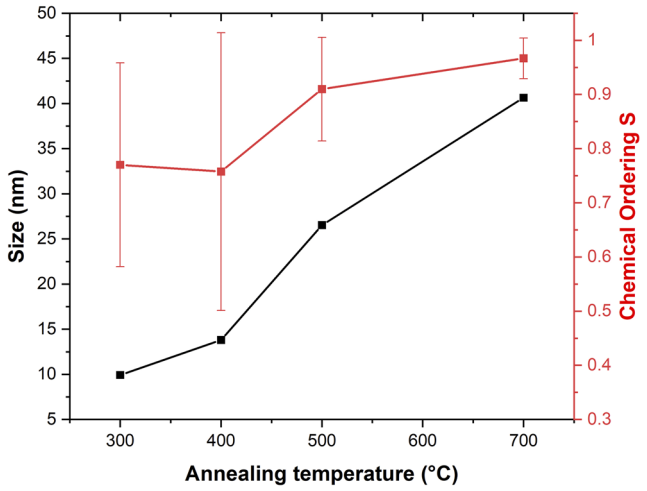

FIG. 2. Calculated sizes and chemical ordering S as a function of annealing temperature. The different data points are connected to guide the eye.

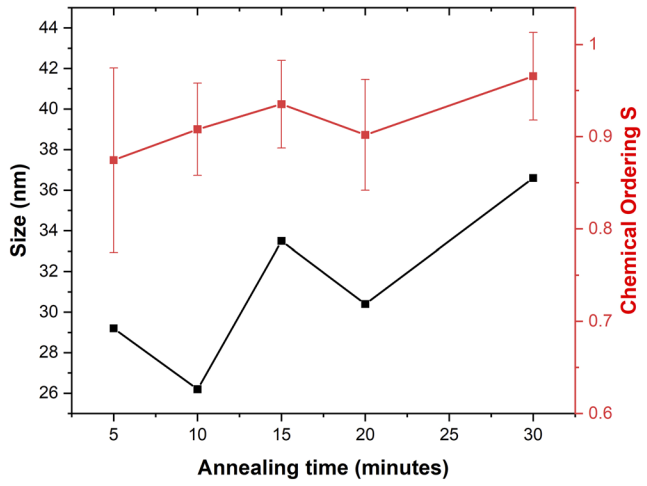

FIG. 4. Calculated particle size and chemical ordering *S* as a function of annealing time at 700°C.

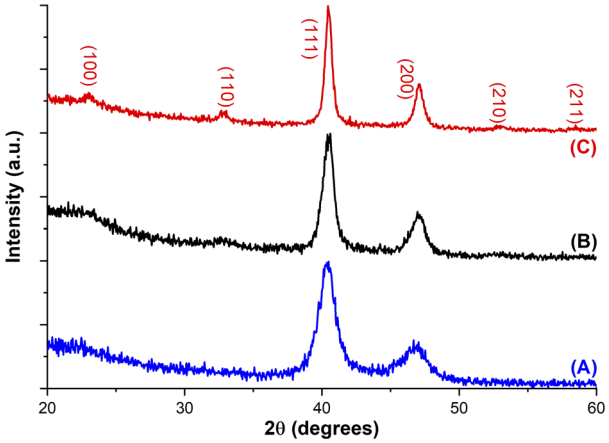

FIG. 5. Comparison of the XRD patterns of as-synthesized nanoparticles obtained from 3 different reactions: (A) no iodine used, (B) standard reaction and (C) 3:1 Fe:Pt precursor ratio, 2 ml TO/18 ml OAm solvent ration, reaction time of 3 hours. Indexed peaks are those of $L1_2$ $FePt_3$.

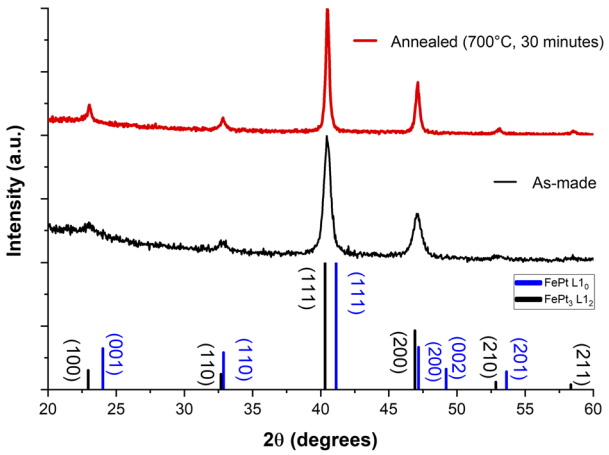

FIG. 6. XRD pattern of as-made nanoparticles and nanoparticles annealed at 700°C for 30 minutes in a reaction where a 3:1 Fe:Pt precursor ratio and 2 ml/18 ml TO/OAm solvent ratio were used.

TABLE I. Comparison of as-made nanoparticles and nanoparticles at 700°C for 30 minutes from both standard reaction and reaction C (3:1 Fe/Pt precursor ratio, 2 ml/18 ml TO/OAm ratio).

Reaction	Sample	Estimated size (nm)	Degree of ordering
Standard reaction	As-made	11.7	0.82 ± 0.17
Standard reaction	Annealed	40.6	0.96 ± 0.04
3:1 Fe/Pt ratio	As-made	15.0	0.86 ± 0.11
3:1 Fe/Pt ratio	Annealed	34.0	0.92 ± 0.06

evidenced for example by the weaker intensity (001) and (110) peaks. Annealing the as-made nanoparticles increased the particle size, as shown by a sharpening of the $L1_2$ $FePt_3$ peaks, as heat treatment promotes the transformation of the disordered fcc $FePt_3$ phase into the ordered $L1_2$ $FePt_3$ phase. No $L1_0$ phase was detected in the as-made and annealed nanoparticles, as indicated by the absence of resolved (002) and (200) peaks of the fct-FePt phase.

The particle size estimated using the Scherrer equation confirmed a general increase with annealing temperature, as shown in Figure 2. The degree of ordering S was calculated for the different alloys to better quantify the structural transformation after annealing. The following expression is used for S:[15]

$$S^2 = \frac{I_{110}/I_{111}}{I^O_{110}/I^O_{111}} \quad (1)$$

I_{110} and I_{111} are the measured peak intensities of the (110) and (111) peaks respectively in the XRD data, whereas I^O_{110} and I^O_{111} are the corresponding peak intensities of the fully ordered $L1_2$ $FePt_3$ phase. The increase in chemical ordering S with annealing temperature plotted in Figure 2 shows that higher annealing temperatures enhance the transformation to the ordered $L1_2$ $FePt_3$ phase.

The structural transformation as a function of annealing time was also investigated in samples made from a different reaction (10 ml/10 ml TO/OAm solvent ratio). Figure 3 shows the XRD data of particles from this reaction annealed at 700°C for different durations. The particle size was estimated using the Scherrer equation and the chemical ordering S estimated as before using Eq. (1) (Figure 4).

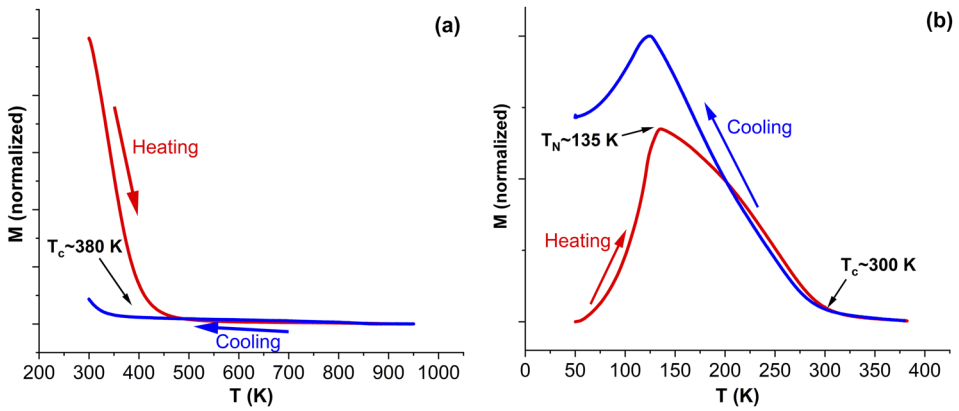

FIG. 7. M vs T of (a) as-made sample and (b) nanoparticles annealed at 700°C for 30 minutes.

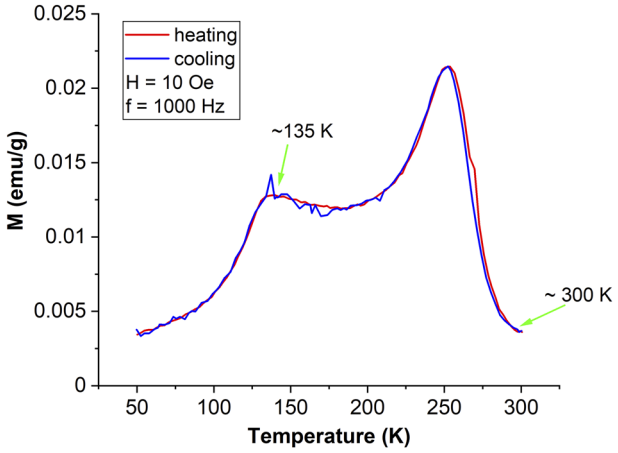

FIG. 8. AC susceptibility measurement on sample annealed at 700°C for 30 minutes.

In general, annealing for longer times produces larger nanoparticles. The chemical degree of ordering also increases, and the effect is more visible for longer annealing times.

We have also investigated the effect of iodine and using different precursor and solvent ratios on the crystal structure of the as-made particles. In Figure 5, the XRD pattern for the reaction where no iodine is used indicates that the nanoparticles are mostly in the disordered fcc $FePt_3$ structure (blue curve, reaction A). This suggests that one important effect of using iodine is that it enhances the formation of the $L1_2$ $FePt_3$ phase.

Reaction C was performed by using a 3:1 Fe:Pt precursor ratio, a 2 ml TO/18 ml OAm solvent ratio and a reaction time of 3 hours. The XRD pattern in Figure 5 shows clearly that tripling the amount of $Fe(acac)_3$ used did not produce the $L1_o$ phase (reaction C). This is in sharp contrast to previously reported work done where the stoichiometric ratio of Fe and Pt in Fe-Pt nanoparticles is controlled by varying the amounts of the Fe and Pt precursors.[16] It may be possible that our choice of precursors combined with the presence of halide ions in the reaction mixture favor the formation of the $L1_2$ $FePt_3$ phase and may provide a pathway of guaranteeing the formation of the $L1_2$ $FePt_3$ phase with different size distributions.

We also observed that the $L1_2$ $FePt_3$ particles made with reaction C in Figure 5 had larger sizes without the need of any post annealing. Annealing at 700°C for 30 minutes also increased the size as indicated by the sharper peaks in the XRD pattern of the annealed $FePt_3$ particles from Figure 6.

The sizes of the as-made nanoparticles and nanoparticles annealed at 700°C for 30 minutes from reaction C were compared to those from the standard reactions (Table I). The data confirms that larger as-made nanoparticles with a higher degree ordering are obtained in the modified reaction, compared to the standard reaction. This suggests the possibility of producing $L1_2$ $FePt_3$ as-made nanoparticles with a given size distribution and chemical ordering by adjusting the reaction parameters in the future work.

Thermomagnetic measurements were performed at an applied field of 500 Oe on the as-made nanoparticles and nanoparticles annealed at 700°C for 30 minutes from the standard reaction (Figure 7).

The as-made data shows that the disordered $FePt_3$ sample has a Curie temperature close to 380 K. Thermomagnetic measurements on the annealed sample at 700°C for 30 minutes showed a mixture of two magnetic structures; a ferromagnetic phase with Curie temperature of about 300 K and an antiferromagnetic phase with a Néel temperature around 135 K. A physical property measurement system (PPMS) was also used to carry out AC susceptibility measurements on the annealed sample. The AC susceptibility data confirms the transition temperature of about 135 K for the antiferromagnetic transition and the Curie temperature of around 300 K (Figure 8).

The effect of the structural transformation on the magnetic properties of the $FePt_3$ nanoparticles is also seen from the hysteresis loops at 300K and 50 K (Figure 9).

The hysteresis loops at 300 K and 50 K show that the magnetization decreases with increasing annealing temperature, because of the ferromagnetic to antiferromagnetic transition. A non-monotonic change in the coercivity with annealing temperature is observed which can be explained by the mixture of ferromagnetic and antiferromagnetic phases and to increased particle sizes at higher annealing

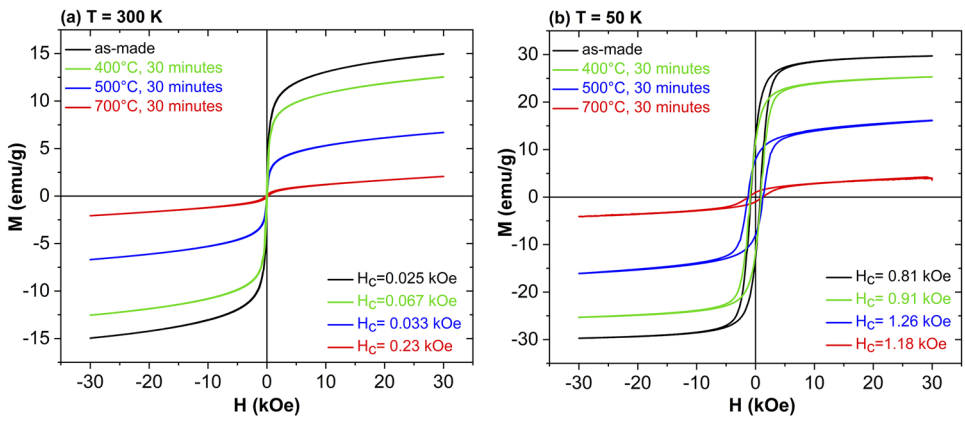

FIG. 9. Hysteresis loop measurements on samples measured at (a) 300 K and (b) 50 K.

temperatures. Our XRD and magnetic data show that annealing at 700°C for 30 minutes results in a very ordered $L1_2$ phase. By annealing at even higher temperatures, the suppression of the ferromagnetic phase within the AFM matrix may be increased further.[14]

IV. CONCLUSION

In conclusion, we report a chemical approach to synthesize $L1_2$ $FePt_3$ nanoparticles using iodine. The as-made nanoparticles were found to have the disordered fcc $FePt_3$ structure and are ferromagnetic with a Curie temperature close to 380 K. Annealing the nanoparticles increased the size and the chemical ordering of the $L1_2$ structure. Nanoparticles annealed at 700°C for 30 minutes shows an ordered $L1_2$ structure with a Curie temperature close to 300 K and an antiferromagnetic phase with a Néel temperature at around 135 K. The use of iodine was found to improve to some extent the formation of the $L1_2$ $FePt_3$ in the as-made nanoparticles. Using a 2 ml TO/18 ml OAm solvent ratio, 3:1 Fe:Pt precursor ratio and a 3 hour reaction time was found to produce larger sized and more ordered $L1_2$ $FePt_3$ as-made nanoparticles. Future work is focused on finding the optimum reaction conditions to directly obtain a highly ordered and monodispersed $L1_2$ $FePt_3$ nanoparticles without the need for any additional heat treatment.

ACKNOWLEDGMENTS

This work was supported by DOE Grant FG02-90ER45413.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1]S. Sun, "Recent advances in chemical synthesis, self-assembly, and applications of FePt nanoparticles," Adv. Mater. **18**, 393 (2006).
[2]K. Zhu, Y. Ju, Z. Yang, S. Gao, and Y. Hou, "Magnetic nanomaterials: Chemical design, synthesis, and potential applications," Acc. Chem. Res. **51**, 404–413 (2018).
[3]Q. Li, L. Wu, G. Wu, D. Su, H. Lv, S. Zhang, W. Zhu, A. Casimir, H. Zhu, A. Mendoza-Garcia, and S. Sun, "New approach to fully ordered fct-FePt nanoparticles for much enhanced electrocatalysis in acid," Nano Lett. **15**(4), 2468–2473 (2015).
[4]J. Kim, Y. Lee, and S. Sun, "Structurally ordered FePt nanoparticles and their enhanced catalysis for oxygen reduction reaction," J. Am. Chem. Soc. **132**, 4996–4997 (2010).
[5]Y. Shi, M. Lin, X. Jiang, and S. Liang, "Recent advances in FePt nanoparticles for biomedicine," Journal of Nanomaterials **2015**, 467873.
[6]F. M. Abel, V. Tzitzios, E. Devlin, S. Alhassan, D. J. Sellmyer, and G. C. Hadjipanayis, ACS Applied Nano Materials **2**(5), 3146–3153 (2019).
[7]W. Pei, D. Zhao, C. Wu, Z. Sun, C. Liu, X. Wang, J. Zheng, M. Yan, J. Wang, and Q. Wang, ACS Applied Nano Materials **3**(2), 1098–1103 (2020).
[8]W. Lei *et al.*, Nano Lett. **18**, 7839–7844 (2018).
[9]W. Lei *et al.*, Nanoscale **9**, 12855 (2017).
[10]G. E. Bacon and J. Crangle, Proc. R. Soc. London, Ser. A **272**, 387 (1963).
[11]A. T. Heitsch, D. C. Lee, and B. A. Korgel, J. Phys. Chem. C **114**, 2512–2518 (2010).
[12]S. Maat, O. Hellwig, G. Zeltzer, E. E. Fullerton, G. J. Mankey, M. L. Crow, and J. L. Robertson, Phys. Rev. B **63**, 134426 (2001).
[13]O. Margeat, M. Tran, M. Spasova, and M. Farle, Phys. Rev. B **75**, 134410 (2007).
[14]H. M. Song, W. S. Kim, Y. B. Lee, J. H. Hong, H. G. Lee, and N. H. Hur, J. Mater. Chem. **19**, 3677–3681 (2009).
[15]Y. K. Takahashi, T. Koyama, M. Ohnuma, T. Ohkubo, and K. Hono, J. Appl. Phys. **95**(5), 2690 (2004).
[16]Y. Liu, Y. Jiang, X. Zhang, Y. Wang, Y. Zhang, H. Liu, H. Zhai, Y. Liu, J. Yang, and Y. Yan, Solid State Chem. **209**, 69–73 (2014).