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High-pressure synthesis of giant magnetostrictive $Pr_xTb_{1-x}Fe_{1.9}$ alloys

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$Pr_xTb_{1-x}Fe_{1.9}$ ($0 \leq x \leq 1$) magnetostrictive alloys with cubic Laves phase have been synthesized by a high-pressure synthesis method. Crystal structure, magnetic properties, magnetocrystalline anisotropy, and the magnetostriction of $Pr_xTb_{1-x}Fe_{1.9}$ ($0 \leq x \leq 1$) alloys are investigated. Composition anisotropy compensation is realized in $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy, which shows low magnetocrystalline anisotropy and a large magnetostriction value ($\lambda_{\parallel}-\lambda_{\perp}=1497$ ppm) at 13 kOe at room temperature. These characters suggest that $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy may be a promising candidate for magnetostriction application. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2387865]

$REFe_2$ (RE=rare earths) giant magnetostrictive compounds, such as Terfenol-D ($Tb_{0.27}Dy_{0.73}Fe_2$), have been widely applied in acoustic transducers, sensors, actuators, etc.[1,2] According to the single-ion model,[3] $PrFe_2$ should generate a larger magnetostriction than $TbFe_2$ and $DyFe_2$ at 0 K and it has the opposite anisotropy sign to $TbFe_2$, so the pseudobinary compounds $Pr_xTb_{1-x}Fe_2$ should be an acceptable compensating system. Owing to the small magnetocrystalline anisotropy of $PrFe_2$,[3] the anisotropy compensation in $Pr_xTb_{1-x}Fe_2$ system requires a high Pr concentration. In most previous work, an unanticipated noncubic structure appeared when the composition of Pr was beyond 20% (Ref. 3) or 25% (Ref. 4) and, therefore, the anisotropy compensating could not be reached in the $Pr_xTb_{1-x}Fe_2$ system under ambient condition. In the past several years, much attention has been paid to enhance the cheaper rare earth Pr content in magnetostrictive materials.[5–8] As an example, progress was made when boron atoms were introduced in the (Pr, RE) Fe_2 system; however, the Pr content should not exceed 30 at.% in order to obtain single Laves phase.[8] So far, a good method to prepare high Pr content of magnetostrictive materials is still desired. In this letter, $Pr_xTb_{1-x}Fe_{1.9}$ ($0 \leq x \leq 1$) polycrystalline alloys with cubic Laves phase are synthesized by a high-pressure synthesis method and the anisotropy composition compensation is realized at $x=0.9$.

Ingots with $Pr_xTb_{1-x}Fe_{1.9}$ ($0 \leq x \leq 1$) stoichiometric composition were prepared by melting the constituent metals in a magnetocontrolled arc furnace in a high-purity argon atmosphere. The purities of the constituents are 99.9% for Tb and Pr and 99.8% for Fe. The as-cast ingots (about 10 mm in diameter and 2 mm in thickness) were wrapped in tantalum foils and pressed into a graphite pipe heater with the shape of cylinder. The heater was then pressed to 6 GPa by a Hall-type hexahedral anvil press and heated to 1173 K for 30 min. Then the samples were annealed between 623 and 723 K for 120 h in vacuum quartz capsules. Conventional x-ray diffraction (XRD) analysis was carried out using Cu $K\alpha$ radiation with a Rigaku D/Max-gA diffractometer. The Curie temperatures were measured by a quantum design superconducting quantum interference device (SQUID) magnetometer at fields of 1 kOe. Magnetization curves at room temperature were measured by a SQUID magnetometer at fields up to 65 kOe. The linear magnetostriction was measured using standard strain-gauge technique in directions parallel ($\lambda_{\parallel}$) or perpendicular ($\lambda_{\perp}$) to applied magnetic fields up to 13 kOe at room temperature.

Figure 1 shows XRD patterns for $Pr_xTb_{1-x}Fe_{1.9}$ with different Pr concentrations. It is found that all the polycrystalline alloys consist predominantly of cubic Laves phase with $MgCu_2$-type structure, coexisting with a minor of impurity phases, i.e., hcp-(Pr, Tb). For the $RE-Fe_2$, the ideal radius ratio of RE and Fe for the formation of a Laves phase is 1.225.[9] It is known that Pr is the largest atom among all the lanthanide elements except Ce. The large size of the Pr atom precludes the ambient pressure synthesis of the $Pr_xTb_{1-x}Fe_{1.9}$ alloys when the Pr concentration exceeds about 0.2.

The dependence of the lattice parameter (a) on the Pr concentration obtained from the XRD data is shown in Fig. 2(a). An approximate linear increase with stoichiometric Pr concentration from 0.0 to 1.0 is found, as expected from Vegard's law:

$$a = xa_1 + (1-x)a_2,$$

where a_1 and a_2 are the lattice parameters of $PrFe_{1.9}$ and $TbFe_{1.9}$, respectively. The lattice parameter increases slowly with increasing Pr concentration in $Pr_xTb_{1-x}Fe_{1.9}$ system due to the fact that Pr has a larger ionic radius than Tb.

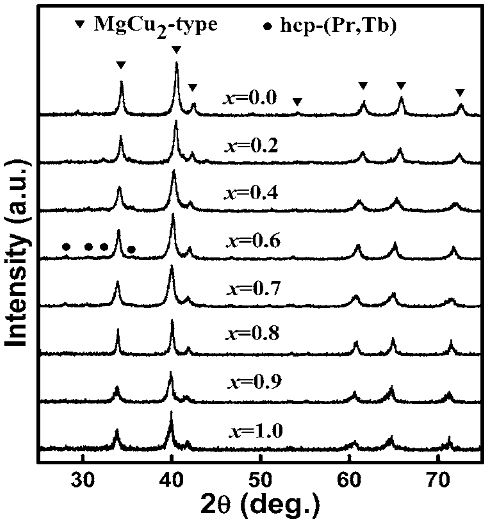

FIG. 1. XRD patterns of the $Pr_xTb_{1-x}Fe_{1.9}$ alloys with different x.

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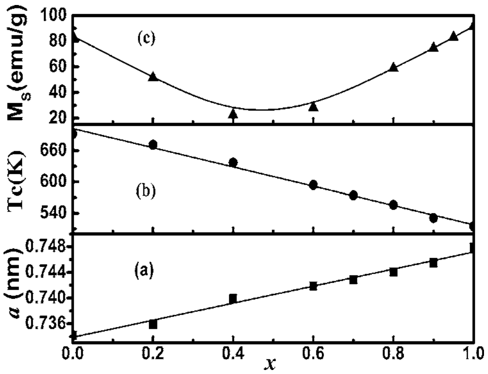

FIG. 2. Lattice parameter *a* (a), the Curie temperature T_C (K) (b), and the saturation magnetization M_s (c) as a function of Pr concentration.

The thermomagnetic curves of the sample with $x=0.9$ are shown in Fig. 3. With temperature increasing the magnetization decreases sharply and to zero near 551 K where T_c is the Curie temperature of the $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ phase, and then the magnetization increases slowly from 650 K due to oxidation of the alloy and the formation of a little amount of α-Fe with temperature increasing. As the temperature turns back from 770 K, the magnetization goes up sharply from 550 K and coincides with heating process magnetization curves, which indicates that the $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ phase does not decompose below 770 K. Compared with the decomposed temperature (681 K) of the $PrFe_{1.9}$ phase in our experiment, the $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ phase is more stable with increasing Tb content. The decomposed temperatures of the $Pr_xTb_{1-x}Fe_{1.9}$ with $x \leqslant 0.9$ are all higher than 770 K. Figure 2(b) shows the variation of Curie temperature with the Pr concentration for $Pr_xTb_{1-x}Fe_{1.9}$ compounds. It is found that the Curie temperature decreases almost linearly with increasing Pr content.

The magnetization curves for $Pr_xTb_{1-x}Fe_{1.9}$ with various compositions are shown in Fig. 4. The saturation magnetizations were deduced from M/H vs M plots. The saturation magnetizations (M_s) of $Pr_xTb_{1-x}Fe_{1.9}$ compounds as a function of the Pr concentration are shown in Fig. 2(c). It is found that the saturation magnetization decreases with increasing Pr concentration till $x=0.4$ and increases when $x \geqslant 0.6$. Since Fe couples ferromagnetically with Pr and couples antiferromagnetically with Tb respectively, the magnetic moment of $Pr_xTb_{1-x}Fe_{1.9}$ can be described as $\mu_s=(1-x)\mu_{Tb}-1.9\mu_{Fe}-x\mu_{Pr}$. Therefore, the substitution of Tb with Pr leads to the decrease and subsequent increase in saturation magnetization.

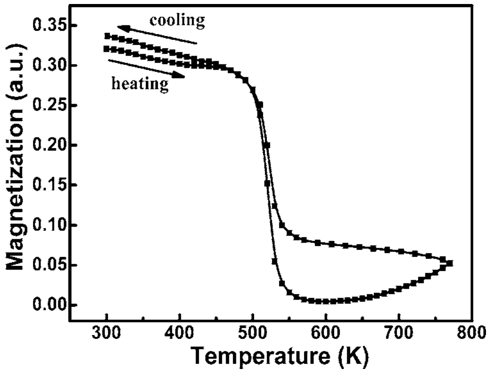

FIG. 3. Magnetization of as $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ a function of temperature at a field of 1 kOe.

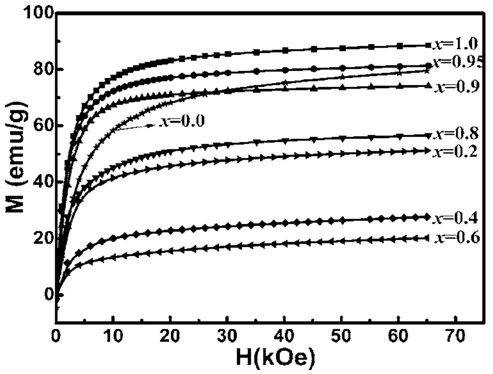

FIG. 4. Magnetization of $Pr_xTb_{1-x}Fe_{1.9}$ alloys at 300 K up to a field of 65 kOe.

Vacuum annealing below the decomposed temperature of the alloys is an effective procedure to improve the magnetostriction of the samples. Considering the different decomposed temperature of $Pr_xTb_{1-x}Fe_{1.9}$ alloys, $PrFe_{1.9}$ and $Pr_{0.95}Tb_{0.05}Fe_{1.9}$ were annealed at 623 K and all the other alloys were annealed at 723 K. The magnetostrictions of all the samples were improved to different extent after annealing. As an example, the magnetostriction value $(\lambda_\parallel-\lambda_\perp)$ of $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy increased from 1228 to 1497 ppm at a magnetic field of 13 kOe. The increase of the magnetostriction of the samples after annealing might be ascribed to the partial removal of the stress in the alloys.

The dependence of magnetostriction $(\lambda_\parallel-\lambda_\perp)$ on the Pr concentration in $Pr_xTb_{1-x}Fe_2$ alloys at various applied magnetic fields is shown in Fig. 5(a). Its behavior is similar to the magnetostriction of $Tb_{1-x}Dy_xFe_2$ alloys.[3] Near $x=0.9$, the magnetostrictions exhibit a peak at low fields, reflecting that the $Pr_xTb_{1-x}Fe_{1.9}$ system is an anisotropy compensation system and the compensating point is just around this point,

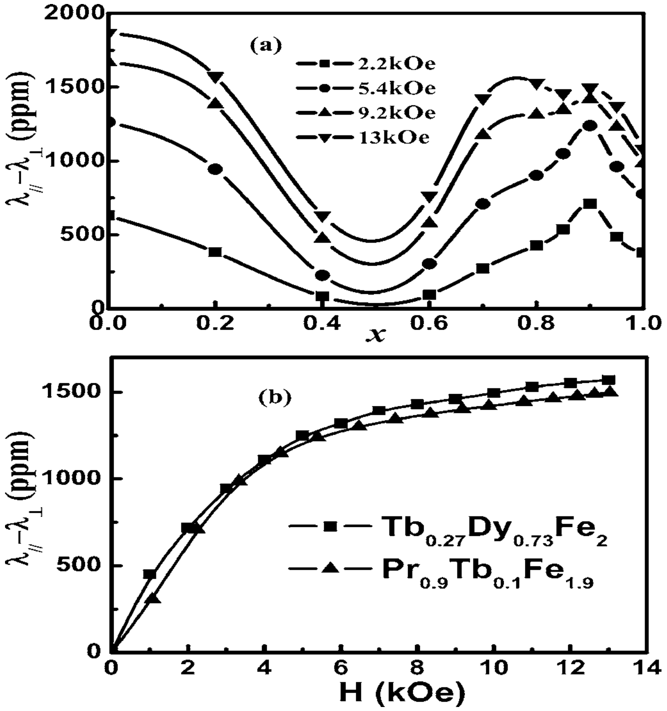

FIG. 5. Magnetostriction at different fields for $Pr_xTb_{1-x}Fe_{1.9}$ alloys (a) and magnetostriction for $Tb_{0.27}Dy_{0.73}Fe_2$ [reported by Wu *et al.* (Ref. 11)] and $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ (b).

which is consistent with the earlier prediction.[10] In comparison with $Tb_{0.27}Dy_{0.73}Fe_2$, the compensating point in $Pr_xTb_{1-x}Fe_{1.9}$ is at Tb=0.1 which results from the fact that $PrFe_{1.9}$ has a lower magnetocrystalline anisotropy than $TbFe_2$. We can note from Fig. 5(b) that the magnetostriction of $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy approach to saturation at 13 kOe and shows a large magnetostriction value ($\lambda_\parallel - \lambda_\perp = 1497$ ppm), which is almost comparable to the magnetostriction of polycrystalline $Tb_{0.27}Dy_{0.73}Fe_2$ alloy. Furthermore, this alloy, which is near the anisotropy compensation point, should have a small anisotropy similar to $Tb_{0.27}Dy_{0.73}Fe_2$. Attention should be paid to the $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy that mainly contains light rare earth Pr, which is much cheaper than $Tb_{0.27}Dy_{0.73}Fe_2$ alloy.

In conclusion, we have synthesized $Pr_xTb_{1-x}Fe_{1.9}$ ($0 \leq x \leq 1$) magnetostrictive alloys with cubic Laves phase by a high-pressure synthesis method. $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy shows low magnetocrystalline anisotropy and a large saturation magnetostriction value at room temperature, which may be a promising candidate for magnetostriction application. Considering the cheaper Pr and large magnetostriction of $Pr_{0.9}Tb_{0.1}Fe_{1.9}$ alloy, the present study may open an avenue in the field of Pr-based magnetostrictive materials.

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