



## Regular article

Magnetic properties of Mo-stabilized bulk Fe<sub>3</sub>B magnet

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## ABSTRACT

Fe<sub>3</sub>B is a metastable high temperature phase and exists in orthorhombic and tetragonal structures. Here, we report on synthesis, structural and magnetic properties of tetragonal (*P*<sub>4</sub>/*n*) Fe<sub>3</sub>B stabilized by a very small substitution of Mo (1–3 at.%) for Fe. The (Fe<sub>0.98</sub>Mo<sub>0.02</sub>)<sub>3</sub>B compound possesses a high Curie temperature of 780 K and high saturation magnetization of 175 A·m<sup>2</sup>/kg (1.60 T). Magnetocrystalline anisotropy field of around 0.8 T and anisotropy energy of 340 kJ/m<sup>3</sup> have been determined for magnetically-oriented fine particles of (Fe<sub>0.98</sub>Mo<sub>0.02</sub>)<sub>3</sub>B.

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Permanent magnets are essential components used in a range of energy efficient devices for applications in energy, conversion, data storage and magnetic cooling [1,2]. Performance of a permanent magnet is characterized by the maximum energy product and the operating temperature range. Nd<sub>2</sub>Fe<sub>14</sub>B and SmCo<sub>5</sub> are considered as high performance permanent magnets, however these materials utilize significant amounts of expensive and sometimes scarce rare-earth (RE) elements. Intensive research on the search of new types of permanent magnets possessing reasonably good magnetic properties but employing reduced or no use of the RE-elements is in progress worldwide [3,4]. This type of magnet could close the huge gap in performance between low cost ferrite and high energy density NdFeB. There are two ways to achieve this objective. First, by fabricating two phase (magnetically-hard and magnetically-soft/-semi-hard phases) nanocomposite permanent magnets and second, by improving the magnetocrystalline anisotropy of high magnetic moment (magnetically-soft) materials [3–8].

Fe<sub>3</sub>B is an interesting system because of its large saturation magnetization and reasonably strong magnetic anisotropy. It has a potential to be used as magnetic soft/semi-hard phase for the fabrication of the two phase nanocomposite permanent magnets [3,9]. However, Fe<sub>3</sub>B is a metastable high temperature phase and has been reported to be present along with Nd<sub>2</sub>Fe<sub>14</sub>B in melt spun ribbons of approximate composition Nd<sub>4</sub>Fe<sub>78</sub>B<sub>18</sub>. The Fe<sub>3</sub>B compound is reported to exist in orthorhombic (*Pnma*) and tetragonal (*P*<sub>4</sub>/*n* and *I*-4) structures at high temperature and decomposes into Fe<sub>2</sub>B and Fe below 1420 K [10, 11]. The tetragonal phase is stable in only very narrow temperature

interval of 1420–1450 K, whereas the orthorhombic modification exists only between 1450 and 1480 K [12–14]. Coene *et al.* [11] has prepared the Fe<sub>3</sub>B compound by melt spinning of Fe<sub>76</sub>B<sub>24</sub> followed by annealing at 470 °C, however the compound was not a single phase. Around 20% of orthorhombic Fe<sub>3</sub>B and 3% of α-Fe were detected along with tetragonal Fe<sub>3</sub>B main phase. Coene *et al.* has also investigated the magnetic properties of these two phase ribbons by means of Lorentz transmission electron microscopy and magnetization measurements. Their studies revealed an easy-plane magnetocrystalline anisotropy, with [110] axis being the easy magnetization direction, and an anisotropy field of 0.5 T for tetragonal Fe<sub>3</sub>B phase [11]. To the best of our knowledge there are no reports on the single phase Fe<sub>3</sub>B system. In this work, we report on stabilizing Fe<sub>3</sub>B compound in tetragonal symmetry (*P*<sub>4</sub>/*n*) with very small substitution of Fe by Mo (~2 at.%) atoms, and discuss the magnetic properties of the compound.

(Fe<sub>1-x</sub>Mo<sub>x</sub>)<sub>3</sub>B (*x* = 0.0–0.1) samples were prepared by melting high-purity elements (Fe-99.99%, Mo-99.99%, B-99.999%) in an arc furnace under a purified argon gas atmosphere. The resulting ingots were suction-casted from melt into thin rectangular ingots of thickness 0.5 mm. Suction-casting is a method of rapid solidification used to obtain a homogeneous elemental distribution in the solid. The ingots were then homogenized by heat treating under vacuum at 1050 °C for two weeks and then subsequently quenched in water. The ingots were cut and polished for optical microscopy and scanning electron microscopy (SEM). The phase purity and the elemental composition were checked with optical microscopy, SEM in back scattered electron (BSE) contrast and energy-dispersive X-ray spectroscopy (EDX) analysis. The content of B was assumed to be constant at 25 at.%, as it is not detectable by the EDX. The ingots (after removing the outer layer) were grounded down to fine particles of size less than 20 μm. X-ray diffraction (XRD) was carried out on a Stoe Stadti P powder diffractometer in transmission

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mode with Mo-K $\alpha_1$  radiation. Phase matching and unit-cell refinements were done using *FullProf/WinPLOTR* suite [15,16]. Magnetic measurements were performed using commercial vibrating sample magnetometers, Lake Shore 7400 Series and Quantum Design PPMS-14. Samples for isothermal magnetization measurements were prepared by imbedding the powder particles in paraffin-wax in a capsule. The powder particles of size below 20  $\mu\text{m}$ , assumed to be single crystalline, were aligned in molten paraffin-wax using an orientation field of 1.8 T. Rotation-alignment method described by Wang *et al.* [17] was followed for the alignment of the particles. Curie temperature ( $T_C$ ) was determined using two-tangent method from thermomagnetic curves,  $M(T)$ , of small piece of the ingot in presence of a magnetic field of 0.1 T.

Diffraction patterns of  $(\text{Fe}_{1-x}\text{Mo}_x)_3\text{B}$  samples with  $x = 0, 0.02$  and  $0.1$  annealed at 1050  $^\circ\text{C}$  are displayed in Fig. 1. According to the analysis of the diffraction patterns, the sample without Mo ( $x = 0$ ) presents two phases consisting of  $\text{Fe}_2\text{B}$  and Fe. Addition of a small amount of Mo ( $x = 0.02$ ) resulted in stabilization of the metastable  $\text{Fe}_3\text{B}$  phase with tetragonal crystal structure (space group  $P4_2/n$ ). It was possible to stabilize the  $\text{Fe}_3\text{B}$  phase with even  $x = 0.01$ , however small amount of  $\text{Fe}_2\text{B}$  was observed in the diffractogram. Increasing the Mo content above  $x = 0.03$  resulted in the formation of tetragonal  $\text{FeMo}_2\text{B}_2$  phase along with the  $\text{Fe}_3\text{B}$  main phase. The presence of  $\text{FeMo}_2\text{B}_2$  phase is depicted in the XRD pattern for  $x = 0.10$  in Fig. 1. These observations indicate that the metastable  $\text{Fe}_3\text{B}$  structure can be stabilized by around 2 at.% Mo substitution for Fe. The refined lattice parameters of the tetragonal  $(\text{Fe},\text{Mo})_3\text{B}$  phase in samples with different  $x$  values are summarized in Table 1, confirming the presence of a solid solution over the entire composition range studied. Within experimental error, it can be seen from Table 1 that both lattice parameters increase with increasing Mo content. Such a change in cell parameters can be attributed to a larger atomic size of Mo atoms compared to that of Fe atoms.

A similar  $\text{Fe}_3\text{B}$  type compound  $\text{Fe}_{13}\text{Mo}_2\text{B}_5$  (i.e.  $(\text{Fe}_{1-x}\text{Mo}_x)_3\text{B}$  with  $x = 0.133$ ) having tetragonal crystal structure ( $P4_2/n$  #86) has been reported by Haschke *et al.* [18]. The  $\text{Fe}_{13}\text{Mo}_2\text{B}_5$  compound was also synthesized in framework of our study and the suction casted alloy was annealed at 1050  $^\circ\text{C}$  for one week. However, on contrary we have found that this compound ( $x = 0.133$ ) decomposes into  $\text{Fe}_2\text{B}$  and  $\text{FeMo}_2\text{B}_2$  with small fraction of  $\text{Fe}_3\text{B}$ . Morphological analysis of the sample with  $x = 0.02$  performed by polarized light microscope and SEM are shown in Figs. 2 (a) and 2 (b), respectively. Thin layers on the surfaces of ingots which were rich in  $\text{Fe}_2\text{B}$  and Fe, and formed basically due to partial B evaporation. This layer was removed by grinding and only the inner part of the ingots was used for various characterizations. As can be seen in Figs. 2 (a) and 2 (b), the inner part of the ingots is single phase. The composition of different samples was confirmed by EDX for Mo and Fe atoms only as the B is too light to be accurately detected by this technique. The amounts of Mo and Fe detected by EDX were

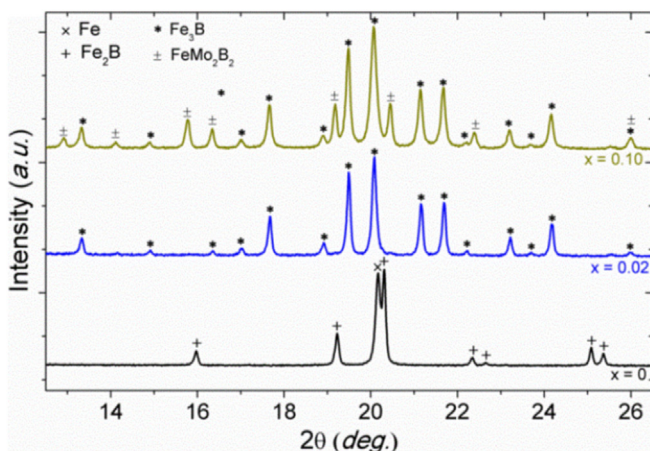


Fig. 1. XRD patterns of  $(\text{Fe}_{1-x}\text{Mo}_x)_3\text{B}$ ,  $x = 0, 0.02$  and  $0.10$ .

Table 1

Lattice parameters of tetragonal  $(\text{Fe},\text{Mo})_3\text{B}$  phase in  $(\text{Fe}_{1-x}\text{Mo}_x)_3\text{B}$  samples with different  $x$  values.

$x$	$a$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )
0.01	8.632(1)	4.308(1)
0.02	8.636(1)	4.309(1)
0.03	8.637(2)	4.312(1)
0.10	8.642(1)	4.313(1)

$1.92 \pm 0.25$  and  $98.08 \pm 0.42$ , respectively, for the sample with  $x = 0.02$ , which is very close to the starting composition.

It is important to note, that the formation of a Boron-depleted surface layer is practically inevitable during long term annealing at 1050  $^\circ\text{C}$ . It means that conventional melt spinning technique is not really a suitable processing route here, at least for preparation of  $\text{Fe}_3\text{B}$  single phase. Indeed, the typical thickness of the melt spun ribbons is of 15–50  $\mu\text{m}$ , while thickness of Boron-depleted layer is of the same order of magnitude. On the other hand, the conventional metallurgy is also not so useful for this purpose, because as-cast bulk  $(\text{FeMo})_3\text{B}$  sample contains rather large inclusions of  $\alpha$ -Fe due to relatively low cooling rate, and it is very difficult to turn this  $\alpha$ -Fe into  $\text{Fe}_3\text{B}$  phase even by annealing the sample for some weeks. Suction casting is a good compromise, because it prevents the formation of large grains of  $\alpha$ -Fe and highly dispersed chemical elements accelerate the diffusion and formation of desired phase.

The temperature dependence of the magnetization in an applied field of 0.1 T is presented in Fig. 3 for  $(\text{Fe}_{0.98}\text{Mo}_{0.02})_3\text{B}$ . The pseudo-binary compound  $(\text{Fe}_{0.98}\text{Mo}_{0.02})_3\text{B}$  is ferromagnetic and undergoes a transition from ordered to paramagnetic state at  $T_C = 780$  K which is very close to the  $T_C$  value of  $\text{Fe}_3\text{B}$  (785 K) reported by Coehoorn *et al.* [3]. However, a small amount of Fe corresponding to the Curie temperature of 1044 K was also observed in the  $M(T)$  curves. The amount of Fe was estimated from the saturation magnetization of Fe by measuring  $M(H)$  curve at 900 K. The fraction of Fe was obtained to be less than 10 wt.% of the total sample weight. The presence of this small amount of Fe could be a secondary phase present in the sample, however no phase contrast was observed in the BSE-SEM image. Furthermore, if a 10 wt.% of Fe was present as secondary phase, it should clearly be visible in the XRD pattern. However, this is not the case for  $x = 0.02$  sample in Fig. 1. These observations indicate a partial decomposition of the  $(\text{Fe}_{0.98}\text{Mo}_{0.02})_3\text{B}$  at high temperature which leads to the presence of Fe seen in the  $M(T)$  curves in Fig. 3.

Fig. 4 (a) shows the isothermal magnetization curves of oriented powder particles measured at room temperature in // and  $\perp$  direction to the orienting magnetic field. The saturation magnetization for  $x = 0.02$  sample is slightly lower as compared to that of pure  $\text{Fe}_3\text{B}$  sample,  $x = 0$  (193  $\text{A}\cdot\text{m}^2/\text{kg}$ ) which is basically a combination of  $\text{Fe}_2\text{B}$  and Fe. A room temperature saturation magnetization of 175  $\text{A}\cdot\text{m}^2/\text{kg}$  (1.60 T) was obtained for  $(\text{Fe}_{0.98}\text{Mo}_{0.02})_3\text{B}$ ,  $x = 0.02$  sample which is slightly lower than the saturation magnetization for pure  $\text{Fe}_3\text{B}$  phase (1.62 T) reported by Coene *et al.* This slight reduction in saturation magnetization is expected due to the non-magnetic Mo atoms. The type of magnetocrystalline anisotropy (easy-axis/-plane) of  $(\text{Fe}_{0.98}\text{Mo}_{0.02})_3\text{B}$  was checked by carrying out a magneto-optic Kerr imaging on a large polished surface (consisting of  $\sim 100$  grains) and by measuring the demagnetization curves in different directions in the plane of the alignment field. There was no magnetic domain contrast visible in the Kerr images, implying the presence of easy-plane anisotropy, which was also observed in the demagnetization curves measured in different directions. Additionally, an easy-plane nature of magnetic anisotropy in tetragonal  $\text{Fe}_3\text{B}$  has been reported by Coene *et al.* [11], observed with the help of Lorentz transmission electron microscopy. This observation indicates that the substitution of Mo for Fe in  $\text{Fe}_3\text{B}$  does not influence the nature of magnetic anisotropy. Room temperature anisotropy energy was determined by calculating the area between the // and  $\perp$

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