Nb-substitution effects in half-metallic double perovskite $\text{Ba}_2\text{FeMoO}_6$

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Abstract. We studied the structural, transport and magnetic properties in a half-metallic double perovskite $\text{Ba}_2\text{FeMo}_{1-x}\text{Nb}_x\text{O}_6$ with $0 \leq x \leq 1$. The observed systematic evolution of the non-metallic upturn with $x$ in the resistivity suggests that the substitution of $\text{Nb}^{5+}$ ($4d^0$) for $\text{Mo}^{5+}$ ($4d^1$) diminishes the spin-polarized carriers. In addition, we observed a linear decrease of the Curie temperature $T_C$ with $x$. It seems that $T_C$ continuously reaches 0 K at $x = 1.0$, where the end material is a paramagnet with antiferromagnetic spin correlations. These results clearly indicate that the decrease of carrier electrons with the substitution gradually destroys the ferromagnetism. $\text{Ba}_2\text{FeMo}_{1-x}\text{Nb}_x\text{O}_6$ is possibly a promising material to determine the mechanism of ferromagnetism in the double perovskites.

1. Introduction

Ordered double perovskite (DP) oxides $A_2BB'O_6$ ($A$: alkaline-earth or rare-earth elements, $B, B'$: transition-metal elements) consist of alternative arrangement of $ABO_3$ and $AB'O_3$ perovskite units. The characteristics of DP oxides are half-metallicity and ferromagnetism with Curie temperature $T_C$ higher than room temperature (RT) [1]. In addition, a large low-field magnetoresistance, due to intergrain tunneling, even at RT, makes the DP oxides promising materials for spintronics [2].

The electronic state near the Fermi level in half-metallic $\text{A}_2\text{FeMoO}_6$, where $A$ is a divalent cation such as $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$, is characterized by localized $\text{Fe}^{3+}$ spins in the majority spin state ($3d^5$: $S = 5/2$) and negative spin-polarized conduction electrons ($t_{2g}$) in the hybridized Fe and Mo orbitals [3]. Theoretically, stabilization of ferromagnetism in the DP oxides has been addressed by the double exchange model [4] or the energy gain model based on the Mo-Fe hybridization [5].

Because it is considered that the conduction electrons mediate the ferromagnetic correlation between the Fe spins, it is of great interest to investigate how the reduction of carriers causes damage to the ferromagnetic order. In this view, substitution of monovalent Na for the $A$ site has been studied [6]. While $T_C$ slightly decreases with the Na substitution, this substitution is unable to completely destroy the ferromagnetic order because of its solubility limit. In this paper, we will report on effects of the Nb substitution for Mo of the $B'$ site in $\text{Ba}_2\text{FeMoO}_6$. Here, the substitution of $\text{Nb}^{5+}$ ($4d^0$) for $\text{Mo}^{5+}$ ($4d^1$) acts just to diminish the spin-polarized carriers [7].
2. Experiments
Polycrystalline samples of Ba$_2$FeMo$_{1-x}$Nb$_x$O$_6$ were prepared by conventional solid-state reactions. Starting materials were BaCO$_3$, Fe$_2$O$_3$, MoO$_3$, and Nb$_2$O$_5$ each with purity of 99.99%. After preheating, regrinding and pelletizing, specimens were sintered for 12 h in a reduced atmosphere of H$_2$ (5%) + Ar (95%) at 1100 °C for $0 \leq x \leq 0.7$ and at 1200°C for $0.8 \leq x \leq 1.7$.

Powder x-ray diffraction (XRD) (Rigaku) with Cu Kα radiation was performed at RT. Resistivity was measured by a standard four-probe method below RT. Magnetization was investigated by a commercial SQUID magnetometer (Quantum Design) between 5 K and 350 K up to 5T.

3. Results and discussion
Figure 1 shows XRD patterns of Ba$_2$FeMo$_{1-x}$Nb$_x$O$_6$ with $0 \leq x \leq 1$. This indicates that the obtained specimens are almost of single-phase. The diffraction peaks for all samples can be indexed as a cubic $Fm\bar{3}m$ symmetry. The Nb substitution induces no structure change at RT, in agreement with Sr$_2$FeMo$_{1-x}$Nb$_x$O$_6$ [7]. The lattice constant systematically increases from 0.807 nm ($x=0$) to 0.814 nm ($x=1.0$), which is based on the larger ionic size of Nb$^{5+}$ (0.064nm) compared to Mo$^{5+}$ (0.061nm).

A superlattice diffraction peak at $2\theta \sim 19^\circ$, which evidences the alternative order of Fe and Mo(Nb) ions at B/B′ sites [8], is noticeable at least up to $x=0.6$ within our resolution, in agreement with Sr$_2$FeMo$_{1-x}$Nb$_x$O$_6$ [7]. The critical composition of $x$ is twice as large as that for Sr$_2$Fe$_{1+x}$Mo$_{1-x}$O$_6$ [9]. This implies that the double-perovskite atomic order is relatively stable for the Nb substitution.

Figure 1. X-ray diffraction patterns for Ba$_2$FeMo$_{1-x}$Nb$_x$O$_6$ ($0 \leq x \leq 1$) at room temperature.

Figure 2. Temperature dependence of resistivity in Ba$_2$FeMo$_{1-x}$Nb$_x$O$_6$.
gradual valence change from Fe\(^{2.5+}\) in average at \(x = 0\) to Fe\(^{3+}\) at \(x = 1.0\) and no change in Mo\(^{5.5+}\) in average [7]. This suggests that the Nb substitution just removes the carrier electrons.

**Figure 3.** Temperature dependence of magnetization at 2 T for Ba\(_2\)FeMo\(_{1-x}\)Nb\(_x\)O\(_6\).

**Figure 4.** \(T_C\) as a function of the Nb content. Here, the broken line is a guide to eye.

The temperature dependence of magnetization under a field of 2 T is illustrated for various \(x\) in Fig. 3. As one can see, the ferromagnetic behavior is systematically destroyed with increase of \(x\). In this study, \(T_C\) is estimated as the temperature where the derivatives of the magnetization \(dM/dT\) takes a maximum value. The obtained \(T_C\)'s are plotted in Fig. 4, indicating that \(T_C\) linearly decreases with \(x\). The decline of \(T_C\), \(dT_C/dx \sim -340\) K/Nb, is one order of magnitude larger than that for A-site substitution of Na [6]. In addition, it is quite contrast with a result that \(T_C\) of Sr\(_2\)Fe\(_{1+x}\)Mo\(_{1-x}\)O\(_6\) is almost insensitive to the Fe substitution for Mo until the ferromagnetism vanishes away [9]. While we found the ferromagnetic behavior up to \(x = 0.9\), \(M(T)\) for \(x = 1.0\) exhibits the Curie-Weiss behavior with Weiss temperature \(\Theta \sim 50\) K down to the lowest temperature measured, suggesting the antiferromagnetic correlation in the end compound of Ba\(_2\)FeNbO\(_6\). This behavior is different from that in Sr\(_2\)FeMo\(_{1-x}\)Nb\(_x\)O\(_6\) [7], where the ferromagnetic character suddenly disappears at \(x = 0.7\). \(T_C\) in Ba\(_2\)FeMo\(_{1-x}\)Nb\(_x\)O\(_6\) with \(x\) seems to linearly approach 0 K at \(x = 1.0\). This implies that \(T_C\) is proportional to the carrier concentration of \((1-x)\). In another sense, only a few carriers doped to the end insulating compound enable to cause appearance of ferromagnetic order. Therefore, such a decrease of \(T_C\) gives substantial evidence of the strong correlation between the carrier electrons and occurrence of the ferromagnetic order.

Figure 5 shows the magnetization curve \(M(H)\) at 5 K. In case of \(x = 0\), 1 T is large enough to saturate the magnetization. The saturation magnetization is estimated as 3.6 \(\mu_B\) per formula unit. This value is a little smaller than the expected 4 \(\mu_B\) for the ferrimagnetic order of Fe\(^{3+}\) and Mo\(^{5+}\) spins. It is widely recognized that the antisite defects diminish the saturation magnetization because the Fe spins in the Mo site antiferromagnetically couple with the regular Fe spins. In the Nb-substituted samples, in addition to the antisite defects, the enhancement of magnetization should be considered due to the reduction of the negative spin-polarized electrons. Such competitive behaviors could cause the peculiar \(x\)-dependence of saturation magnetization with its maximum at \(x = 0.1\) (Fig.3). The further Nb-substitution above \(x = 0.3\) induces the linear field dependence of \(M\) above 0.5 T along with a larger decrease of the saturation magnetization. Such a feature of spin-canting is also reported in Sr\(_2\)FeMo\(_{1-x}\)W\(_x\)O\(_6\) [10]. The estimated spontaneous magnetization \(M_s\)'s by extrapolation to 0 T are plotted in Fig. 6. \(M_s\)
largely decreases at around $x = 0.6$, where the $H$-linear term is found to be maximum. Therefore, we speculate that the deviation of the saturation magnetization from the expected value is caused not only by the above two factors but also by the spin-canting-like behavior. To understand the systematic changes in the magnetic correlation with carrier concentration could provide a crucial insight to appearance of the ferromagnetism in the DP oxides.

Figure 5. Magnetization curve at 5 K for $\text{Ba}_2\text{FeMo}_{1-x}\text{Nb}_x\text{O}_6$.

Figure 6. Spontaneous Magnetization as a function of the Nb content.

4. Summary
We have investigated the structural, transport and magnetic properties in $\text{Ba}_2\text{FeMo}_{1-x}\text{Nb}_x\text{O}_6$ with $0 \leq x \leq 1$. Judging from superlattice peaks in XRD, the alternative atomic order is relatively stable by the Nb substitution. With increasing $x$, the upturn in $\rho(T)$ at low temperatures is clearly growing. Such a sign of carrier localization suggests a decline of the carrier doping level by the Nb substitution. We found a linear decrease of $T_C$ with $x$, which successively reaches $T_C = 0$ K at $x = 1.0$. This gives substantial evidence of the strong correlation between the carrier electrons and occurrence of the ferromagnetic order. In addition, the linear field dependence of magnetization is induced by the substitution. To understand the evolution of the magnetic correlation with carrier concentration could provide a crucial insight to a controversial mechanism for the ferromagnetism above room temperature in the double perovskite oxides. $\text{Ba}_2\text{FeMo}_{1-x}\text{Nb}_x\text{O}_6$ could be such a key material.

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