

A Report on the ESR and Magnetic Structure of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ ($x = 0.15, 0.22$)

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The electron spin resonance signals of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ have been acquired for two samples of $x = 0.15$ and 0.22 . ESR signal of the sample of $x = 0.15$ clearly shows signal shape change into Dysonian with g -value shift at around 165 K so that the charge ordering temperature can be identified. The general features of ESR signal of the two samples well correlate with magnetic susceptibility measurement and also confirm the validity of former investigations.

Key words : electron spin resonance, g -value, charge ordering

1. Introduction

$\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ is one of the perovskite mixed-valent manganites sometimes called TDMO family materials (T: trivalent, D: divalent) having the property of colossal magnetoresistance, i.e. great reduction of resistivity under existence of magnetic field. The temperature dependences of resistivity and magnetic susceptibility of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ as well as its crystal structure have been closely examined [1, 2].

Magnetic phase of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ is rather complicated

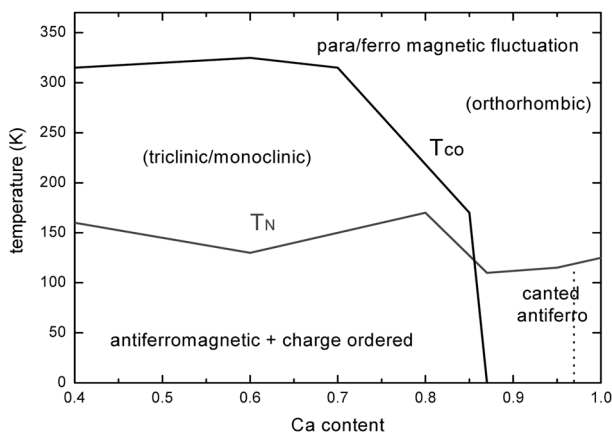


Fig. 1. Summary of phase diagram of the BCMO system (after Woo *et al.*, 2001).

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and is varying with the differing content of bismuth/calcium and also with differing temperature. Although other measurements have been formerly used to identify charge ordering temperature of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$, we found that it can be easily and accurately done by electron spin resonance absorption signal for certain cases such as for $\text{Bi}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$.

It is quite often the case that ESR signals of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ are small at room temperature but they become large enough to be detected at lower temperature particularly around charge ordering temperature and Neel temperature.

2. Experiment

Samples of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ crystal were synthesized by flux method. Mixtures of Bi_2O_3 , CaCO_3 , MnO_2 powders were reacted at 1443 K for several days in air. Compositions were identified by EPMA analysis [3].

Two samples $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.15$ and 0.22 have been examined by electron spin resonance (X-band), magnetic susceptibility measurement, and X-ray diffraction. Temperature ranges for ESR experiment and magnetic susceptibility measurement in this study were 120-400 K and 120-300 K respectively.

3. Result and Discussion

The X-ray diffraction patterns of the powders of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ samples are in Fig. 2. Peak angles of

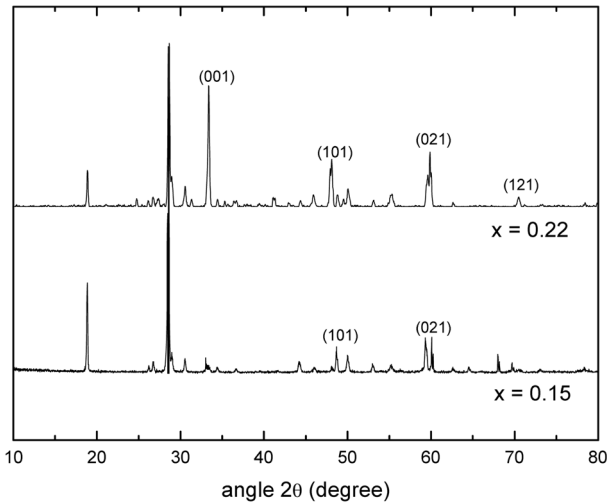


Fig. 2. X-ray diffraction of the samples of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.22$ and 0.15 (index based on pseudo cubic approximation).

$2\theta = 33.4, 48.1,$ and 59.9 are slightly shifted from those of CaMnO_3 and these shifts are due to slight expansion of lattice with Bi content. Two conspicuous peaks of $2\theta = 18.9$ and 28.6 are believed to be associated with planes made of excessive amount of bismuth.

Magnetic susceptibility measurements were done by using Vibrating Sample Magnetometer for temperature range from room temperature down to 120 K and the some major parts are shown in Figure 3-4.

At each given temperature BCMO samples show stable paramagnetic behavior except that the sample of $x = 0.22$ shows a little bit of instability for magnetic field larger than 3000 Oe. Temperature dependences of the magnetic susceptibilities of the two samples in Figure 5 are different from each other and show rather complicated characteristics. It is believed that maximum at 160 K for

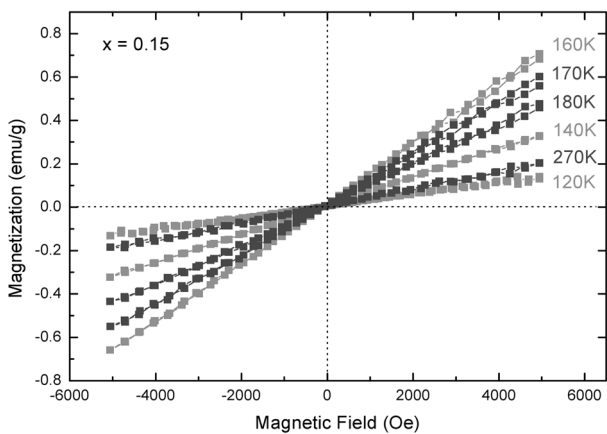


Fig. 3. Induced Magnetizations of the sample of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.15$.

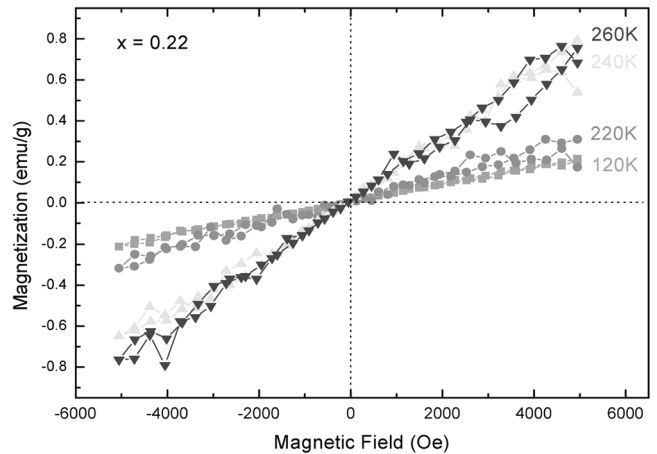


Fig. 4. Induced Magnetizations of the sample of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.22$.

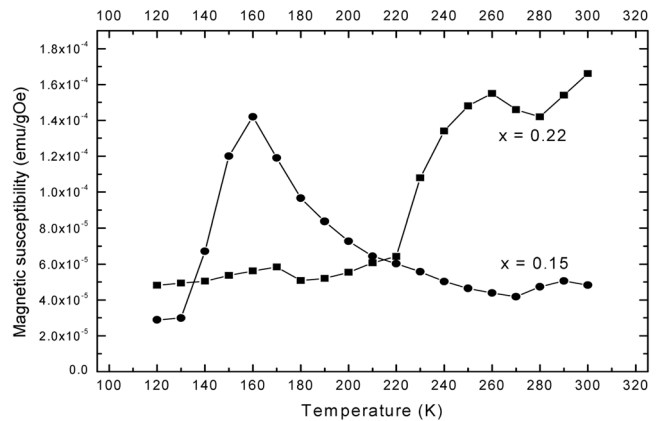


Fig. 5. Temperature dependences of the magnetic susceptibility of $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$.

the sample with $x = 0.15$ is associated with charge ordering as former study. 260 K and 170 K are regarded as charge ordering temperature and Neel temperature of the sample with $x = 0.22$ accordingly.

Electron spin resonance absorption signal of the two samples are in Figure 6 and 7. These are acquired by detecting conventional X-band microwave absorption by the sample under magnetic field at each temperature maintained by controlled nitrogen gas flow with heating.

The ESR differential absorption curves acquired are mostly Lorentian. Evidently close correlation exists between VSM measurement and ESR signal. But they do not exactly match in all temperature range. For the sample of $x = 0.22$, ESR absorption is maximum at $T = 240$ K rather than 250, 260 K and ESR absorption at around room temperature or at $T < 200$ K is smaller than expected from magnetic susceptibility value. For the sample of $x = 0.15$, the signal shape changes from Lorentian for $T > 170$ K

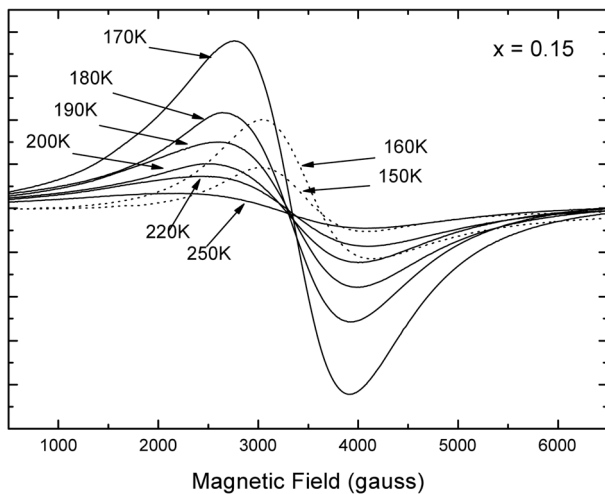


Fig. 6. ESR signals of the sample $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.15$.

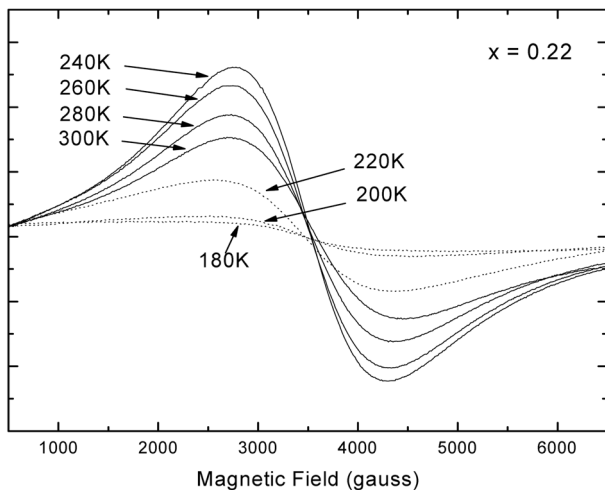


Fig. 7. ESR signals of the sample $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$ with $x = 0.22$.

to Dysonian for $T < 160$ K. And also the g -value shift is evidently shown with this temperature change. From the

BCMO phase diagram after Woo *et al.* it is believed this temperature is related with two phenomena, charge ordering and antiferromagnetic spin ordering. According to their diagram, T_{CO} and T_N are close to each other at this temperature for this sample. From the magnetic susceptibility alone, it is difficult to tell that charge ordering also occurs above/below the Neel temperature. But we can speculate from the ESR signal that charge ordering is coexistent and may be dominant because the Dysonian shape of ESR differential absorption curve is usually acquired for low conducting materials [4]. The charge ordering of the BCMO sample of $x = 0.22$ is quite possibly more gradual at temperature below T_{CO} than that of the other sample. T_N of the sample of $x = 0.22$ is identified as 170 K from magnetic susceptibility curve.

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