



Chapter 1

Introduction

1-1 General overview

The first known magnets were lodestones, stones that are magnetized naturally. From the Greek and Chinese antiquities, the ancient people use lodestones to attract metal and determine direction as compasses. In recent decades, magnets and magnetic materials are the objects of fundamental research and technological application. In these days, magnetic materials are widely used in our daily lives such as ATM, credit cards, PCs, electronic devices and medical utilities. It is said that magnetic materials are becoming more important in the development of modern society. The need for efficient generation and use of electricity is dependent on improved magnetic materials and designs. For example, the telecommunications industry has always pursued the faster data transmission devices, which require development of improved magnetic materials such as transition-metal oxides.

Newly investigated transition-metal oxides, for example, ferroelectric titanates,^[1] colossal magnetoresistance (CMR) manganites,^[2] and high temperature superconducting cuprates,^[3] have attracted great interest in recent years due to their interesting physical properties caused by *d*-orbital electrons. When anisotropic shaped *d*-orbital electrons in solids are bound or localized on the certain atomic site, they have three principle attributions considered: charge, spin, and orbital. First, for the charges, all magnetic phenomena are due to electric charges in motion. Moreover, the strong electron correlation effects induced by the Coulomb interaction between

electric charges are important to understand their physical properties such as colossal magnetoresistance (CMR) (La-doped CaMnO_3)^[2] and high-temperature superconductivity (Cu-doped Sr_2YRuO_6)^[4,5]. Second, for the spins, the magnetic behavior is determined by the alignment of the spins of the d -orbital electrons. For example, $\text{ACu}_3\text{Ti}_4\text{O}_{12}$,^[6-14] CaMnO_3 ,^[15-19] and Sr_2YRuO_6 .^[20,21] are all antiferromagnetic materials that the alignment of nearby spins are anti-parallel below their Néel temperature. Third, for the orbital, the orbital represents the shape of the electron cloud in solid. The ordering of the orbital occasionally plays an important role in the transition-metal oxides. Therefore, d -orbital electrons would cause a variety of phenomena through strong coupling among charge, spin, and lattice dynamics.

1-2 Motivation

The perovskite-like compound $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has been captured much attention for its colossal dielectric response in last six years. In general, the ϵ_1 value of metal is far less than zero. In insulators, the charge is localized and $\epsilon_1 > 0$; materials with a dielectric constant greater than that of silicon nitride ($\epsilon_1 > 7$) are classified as high-dielectric-constant materials. In $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, it revealed very high value of low-frequency dielectric constant $\epsilon_1(100 \text{ kHz}) \sim 8 \times 10^4$ over a wide range temperature range 100 – 600 K.^[14] The almost temperature independent from 100 K to 400 K dielectric constant is desirable for many smaller and faster devices of microelectric applications. However, the $\epsilon_1(100 \text{ kHz})$ drops down to almost 100 below 100 K and above 10^6 Hz . The nature and origin of the colossal dielectric constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and its temperature-dependent behavior are currently great interest for

scientists.

In the mid-1990's, the manganites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.17 \leq x \leq 0.5$ and $x \sim 0.9$) were found to exhibit a very large change in electrical resistance by applying an external magnetic field.^[2,22] This colossal magnetoresistance (CMR) effect has attracted intense and worldwide research in recent years. Zener has first proposed that the electrical conduction and ferromagnetic coupling of the manganites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.2 < x < 0.4$) arise from a double exchange (DE) process.^[23] A. J. Millis *et al.* have shown that the double exchange model failed to account for the sharp drop of the resistivity just below T_C in the CMR effect due to the lack of the consideration of the strong electron-phonon interaction.^[24] They suggest the electron-phonon coupling localizes the electrons in the conduction band as polarons, which result from the interplay of the dynamic Jahn-Teller and double exchange effects.^[24] There have been many other modes proposed to interpret the CMR effect by means of polarons.^[25-27] However, it still needs some consensus to illustrate the nature and origin of the CMR effect. The parent compound of CaMnO_3 without Jahn-Teller distortion is a prototypical and reference material, which can provide the deeper understanding of the manganites.

Recently a number of studies have been focused on the Cu-doped Sr_2YRuO_6 because it becomes a superconductor (15% Cu doping) at an onset temperature of $T_c \sim 45 - 49$ K.^[4] Unlike other superconductors, it has no cuprate planes but only two types of layers, $(\text{SrO})_2$ and $\text{Y}(\text{Ru}_{1-u}\text{Cu}_u)\text{O}_4$. Moreover, it reveals ferromagnetism along a - b planes in one $\text{Y}(\text{Ru}_{1-u}\text{Cu}_u)\text{O}_4$ layer, whose direction of ferromagnetic moments is antiparallel to next $\text{Y}(\text{Ru}_{1-u}\text{Cu}_u)\text{O}_4$ layer. Thus, the ground state of Sr_2YRuO_6 develops an antiferromagnetic structure. The competition between the ferromagnetism and

antiferromagnetic results in the spin-glass behavior in these compounds around 29.25 K.^[4] The interplay between superconductivity and magnetism of Sr_2YRuO_6 are worthy for further study.

The remainder of this paper is divided into four sections. Chapter 2 presents a review of the important previous work of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$, CaMnO_3 , and Sr_2YRuO_6 . In chapter 3, the experimental optical techniques will be described. Chapter 4 shows our experimental results and discussion. Finally chapter 5 is the summary.