

# Chapter 5

## Summary

In summary, we have studied optical reflectance, magnetic properties, and X-ray powder diffraction of ceramic CCTO, NLCTO, and NBCTO, and single-crystalline  $\text{CaMnO}_3$  and  $\text{Sr}_2\text{YRuO}_6$ .

First of all, in the series of ceramic CCTO compounds, the X-ray powder diffraction reveal that the lattice parameters and Ti–O–Ti bond angle of NLCTO and NBCTO are larger than those of CCTO. It should be noted that the replacement of Ca ions with Na and La, or Na and Bi ions causes the lower static dielectric constant and the distorted crystal structure in NLCTO and NBCTO, but do not influence the Néel temperature of NLCTO and NBCTO. The temperature-dependent far-infrared reflectance spectra of three samples exhibit no structural phase transition near  $T_N \sim 26$  K. In the temperature-dependent far-infrared conductivity spectra, we observed the 1<sup>st</sup> phonon modes softening and increasing linewidth and intensity in three samples, but this behavior become smaller in two doping samples. Moreover, the spectral weight and effective charge also increase with decreasing temperature. There is no structural phase transition, and the estimated intrinsic static dielectric constant of CCTO  $\sim 60$  is too small to explain the giant dielectric constant of CCTO. Therefore, we use the IBLC picture as an extrinsic property and combine the effective charge data to interpret the giant dielectric behavior and temperature-dependent dielectric constant of CCTO. Within the IBLC picture, the lower static dielectric constants in two doping sample could arise from their distorted microstructure.

In addition, we observed an antiferromagnetic phase transition of single crystal

CaMnO<sub>3</sub> with  $T_N \sim 125$  K and a weak ferromagnetic moment. No structural phase transition near  $T_N \sim 125$  K was found as well. In the temperature-dependent far-infrared conductivity spectra, the vibrational mode between the Ca atoms and MnO<sub>6</sub> octahedra reveals red shifts and variation in linewidth and intensity near  $T_N \sim 125$  K due to the spin-phonon coupling. It is consistent with the previous temperature-dependent Raman data reported by E. Granado *et al.*<sup>[37]</sup> The absorptions associated with electronic transitions at  $\sim 2.11$  eV,  $\sim 3.48$  eV, and  $\sim 6.3$  eV also remarkably change near  $T_N \sim 125$  K. It is interesting that the thermal energy of the antiferromagnetic phase temperature is too small ( $125 \text{ K} \approx 80 \text{ cm}^{-1}$ ) to affect the electronic absorptions. More detailed theoretical calculations are required for the unequivocal interpretations of the complicated temperature-dependent absorption bands.

Finally, we observed three magnetic phase transitions (antiferromagnetic phase transition:  $T_N \sim 21$  K, spin-glass state:  $T_G \sim 32$  K, and weak ferromagnetic phase transition:  $T_C \sim 135$  K) in Sr<sub>2</sub>YRuO<sub>6</sub>. From optical analysis of the room temperature conductivity spectra at high frequency region, we obtain three essential physical parameters: including (i) the Coulomb correlations  $U$  is  $\sim 2$  eV; (ii) the charge-transfer energy  $\Delta_{p-d}$  is  $\sim 2.82$  eV; and (iii) the crystal-field splitting energy  $10Dq$  is  $\sim 3.37$  eV. More interestingly, the bending mode and stretching mode reveal Fano-type features and noticeable blue shifts near  $T_C \sim 135$  K. Moreover, the interaction between spins and the bending phonon mode is getting stronger with decreasing temperature.

So far, the optical investigations provide us important insights of the physical properties of these oxides. However, some theoretical calculations are desirable to

illustrate what we observed, including the lattice dynamics of all samples, the anomalous temperature-dependent phononic response of  $\text{CaMnO}_3$  and  $\text{Sr}_2\text{YRuO}_6$ , as well as the temperature-dependent electronic transitions of  $\text{CaMnO}_3$ .