

Magnetic and Dielectric Behavior of the Ruthenium Double Perovskite Oxides R_2MRuO_6 ($R=La, Pr$ and Nd , $M=Mg, Co, Ni$ and Zn)

Kenji Yoshii, Naoshi. Ikeda*, Shigeo Mori**, Yasuhiro Yoneda,
Masaichiro Mizumaki***, Hajime Tanida*** and Naomi Kawamura***

Japan Atomic Agency, Mikazuki, Hyogo 679-05148

Fax: 81-791-58-2637, e-mail: yoshiike@spring8.or.jp

*Department of Physics, Okayama University, Okayama 700-8530

Fax: 81-86-251-7810

**Department of Physics, Osaka Prefecture University, Osaka 599-8531

Fax: 81-72-254-9712

***Japan Synchrotron Radiation Research Institute, Mikazuki, Hyogo 679-5198

Fax: 81-791-52-0830

Magnetic and dielectric properties of the ruthenium double perovskites R_2MRuO_6 were studied ($R=La, Pr$ and Nd , $M=Mg, Co, Ni$ and Zn). For $R=La$, the materials with the magnetic M^{2+} ions ($M=Co$ and Ni) showed magnetic ordering and large dielectric constants (~ 5000). On the other hand, for the non-magnetic M^{2+} ions ($M=Mg$ and Zn), magnetic ordering was not observed. In addition, their dielectric constants were found to be small ($\sim 100-200$). Together with the imaginary part and the $\tan\delta$ component of the dielectric response, the large dielectric constants for $M=Co$ and Ni may be related to a smooth response of polar regions. Brief discussion for related materials R_2MRuO_6 with $R=Pr$ and Nd is also described.

Key words: perovskite, ruthenium, oxide, magnetic property, dielectric property

1. INTRODUCTION

Perovskite ruthenium oxides $A_{n+1}Ru_nO_{3n+1}$ ($A=Ca$ and Sr) are known to exhibit some intriguing physical properties, e.g. spin-triplet superconductivity [1]. These properties are believed to originate from a peculiarity of $Ru-4d$ electrons. In course of extensive investigations of full details of the properties, a more complicated perovskite ruthenium system, denoted as a double perovskite, is attracting recent considerable attention. The formula of this system is expressed as R_2MRuO_6 ($R=rare\ earths, M=transition\ metals$), in which the two different transition-metal ions are settled at the crystallographic B -site in the perovskite structure [2-7].

A systematic study of magnetic and electrical properties of this system was recently reported for La_2MRuO_6 with several M elements [8]. The wide variation of the properties with changing M was discussed on the basis of the band structures consisting of $Ru-4d$ and $M-3d$ orbitals.

In this study, we have investigated the magnetic and dielectric properties of some ruthenium double perovskite oxides to obtain further insights into these materials. Their dielectric properties would be interesting in the context of the recent discovery of multiferroic behavior in transition-metal oxides [8]. To compare the results, the investigation was carried out for R_2MRuO_6 with both the magnetic M ions (Co and Ni) and the non-magnetic M ions (Mg and Zn).

2. EXPERIMENTAL

The samples were prepared by a solid-state reaction, as noted previously [5]. Their crystal structures were examined by powder X-ray diffraction (XRD) using $Cu-K\alpha$ radiation. The XRD patterns were refined by the Rietveld method (RIETAN-2000) [9]. The DC and AC

magnetic measurements were carried out by use of a SQUID magnetometer (Quantum Design MPMS). The AC dielectric response was measured below 300 K by an impedance analyzer (HP-4284A) equipped with a He refrigerator. X-ray absorption measurements were also performed to observe the electronic structures. The measurements were carried out at the BL01 and BL38 beamlines using synchrotron radiation of SPring-8.

The other details have been noted elsewhere [5,10].

3. RESULTS AND DISCUSSION

The XRD patterns of all the La_2MRuO_6 samples could be fitted on the assumption of the monoclinic $P2_1/n$ structure, in which the M and Ru atoms are settled with an ordered arrangement [2-7]. As a previous synchrotron-radiation XRD study on La_2NiRuO_6 revealed a partial crystallographic disorder of Ni and Ru [6], we attempted to refine the patterns with changing the occupancies of M and Ru . The refinement showed a small randomness of the occupancies. The randomness was found to be $\sim 1\%$ ($M=Mg$), $\sim 5-6\%$ ($M=Ni$ and Zn) and $\sim 10\%$ ($M=Co$). An example of the obtained fitting parameters for $M=Ni$ is shown in Table 1.

Figure 1 shows the magnetization plotted against the temperature for La_2NiRuO_6 and La_2ZnRuO_6 . La_2NiRuO_6 exhibits antiferromagnetic ordering at ~ 25 K (Fig. 1a), as reported in previous papers [8,10]. Almost the same transition temperature was obtained also for $M=Co$ (not shown) [8]. On the other hand, magnetic ordering is not observed for La_2ZnRuO_6 (Fig. 2b) and La_2MgRuO_6 . The absence of magnetic ordering was also verified by the measurements of isothermal magnetization and AC magnetic susceptibility (Fig. 2b). This behavior is different from that reported previously, in which a ferromagnetic ordering is observed at 165 K [8]. This

Table 1. Fitting parameters obtained from the Rietveld analysis for La_2NiRuO_6 ($a=5.5644(2)$, $b=5.5955(2)$, $c=7.8706(3)$ Å, $R_{wp}=9.54\%$, $R_f=1.48\%$). Isotropic thermal parameters (B) were 0.4-0.5 (Å²) [5].

Atom	Occupancy	x	y	z
La	1	0.0078(5)	0.0424(2)	0.2499(5)
Ni1	0.94(1)	0.5	0	0
Ru1	0.06(1)	0.5	0	0
Ni2	0.06(1)	0.5	0	0.5
Ru2	0.94(1)	0.5	0	0.5
O1	1	0.2815(15)	0.2890(41)	0.0326(44)
O2	1	0.2023(35)	-0.2130(39)	0.0500(41)
O3	1	-0.0876(34)	0.4888(16)	0.2466(42)

difference may arise from some unknown factors (such as heating and cooling rates) and requires further experimental studies of this system.

The antiferromagnetic ordering for $M=Ni$ and Co would be explained in terms of the magnetic interactions between the M^{2+} and Ru^{4+} spins [8]. For La_2NiRuO_6 , the X-ray absorption near edge structure (XANES) spectrum in Fig. 2 provides the valence state of the Ru ion. The spectrum of La_2NiRuO_6 exhibits a similar profile to those of $ARuO_3$ perovskites ($A=Ca$ and Sr) [11], in which the Ru ions are in the 4+ state and are octahedrally surrounded by six oxygen atoms. The peak energies of La_2NiRuO_6 are almost identical to those of

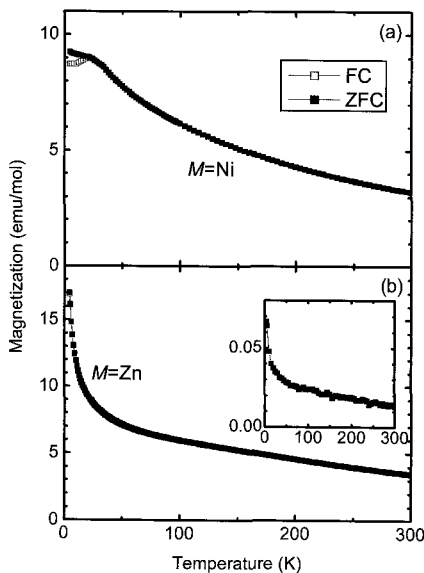


Fig.1. magnetization plotted against temperature for (a) $M=Ni$ and (b) $M=Zn$. The applied magnetic field was 1000 Oe. FC and ZFC stand for the field-cooled and zero-field-cooled sequences, respectively. The inset shows the AC magnetic susceptibility for $M=Zn$. The amplitude and the frequency of the AC applied field were 4 Oe and 100 Hz, respectively.

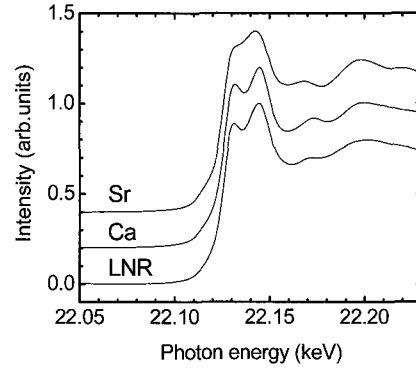


Fig. 2. XANES spectra of La_2NiRuO_6 (LNR), $CaRuO_3$ (Ca) and $SrRuO_3$ (Sr), measured at the Ru- L_3 edge.

$ARuO_3$, which means that the valence of the Ru ion is 4+. The XANES measurements were also carried out at the Ni- K edge (not shown). The absorption edge of La_2NiRuO_6 was nearly the same as that of NiO (Ni^{2+}). These results confirm that the valences of the Ru and Ni ions are 4+ and 2+, respectively [8]. The plausible electronic configuration of Ru^{4+} is $t_{2g}^4e_g^0$, while that of Ni^{2+} is $t_{2g}^6e_g^2$ [8]. Thus, Ru^{4+} has a ferromagnetic coupling with Ni^{2+} through the electron transfer between the e_g orbitals. However, our magnetization measurements indicate that the dominant magnetic interaction is antiferromagnetic. The possible antiferromagnetic interaction exists between the Ni^{2+} ions, caused by the electron transfer between the e_g orbitals [8]. The smaller ferromagnetic interaction is likely ascribable to a weak intra-atomic interaction in the Ru ion, as proposed previously [8].

The origin of the different result of La_2ZnRuO_6 from that in Ref. [8] is unclear at present. However, our result is possibly related to a weakening of magnetic interactions; the magnetic interactions in the Ru sub-array are not strong because of the presence of the non-magnetic Zn^{2+} ion located between the Ru ions. Almost the same results obtained for $M=Mg$ is reasonable, since both Mg^{2+} and Zn^{2+} are non-magnetic ions with almost the same ionic radius [12].

The AC dielectric measurements showed the large dielectric constants of ~ 5000 at room temperature for La_2CoRuO_6 and La_2NiRuO_6 , in which the magnetic M^{2+} ions are contained [10]. On the other hand, La_2MgRuO_6 and La_2ZnRuO_6 showed considerably smaller dielectric constants of 100-200 [10]. For all the oxides, their dielectric constants monotonically decreased with cooling the samples and exhibited no apparent anomaly below 300 K. The results of La_2NiRuO_6 and La_2ZnRuO_6 are demonstrated in Fig. 3, which shows frequency dependence of the dielectric constant, known as a dielectric dispersion. The fitting lines based on the distributed Debye-type dispersion with a parameters α ; this value is regarded as a measure of a distribution of a size of each polar region [13]. Figure 3 also shows that the fitting leads to large α values of $\sim 0.3-0.5$, which

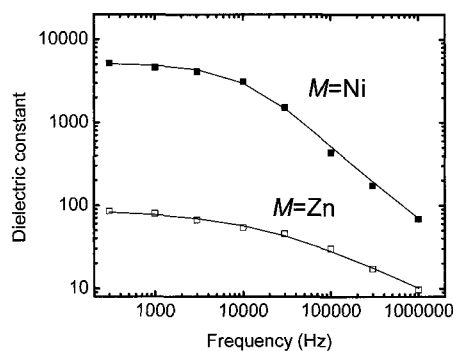


Fig. 3. Dielectric dispersion at 150 K for $M=\text{Ni}$ and $M=\text{Zn}$. The squares and the solid lines stand for the experimental data and the fitting lines, respectively. The α values were calculated to be ~ 0.3 and ~ 0.5 for $M=\text{Ni}$ and $M=\text{Zn}$, respectively.

means a wide distribution of the size of each polar region. This value did not show a clear tendency with changing the M element.

Figure 4 shows the temperature dependence of AC electrical resistivity plotted against the temperature for $\text{La}_2\text{NiRuO}_6$ and $\text{La}_2\text{ZnRuO}_6$, calculated from the imaginary part of the AC dielectric response. Both materials exhibit similar properties to those reported in the reference, i.e., either semiconducting or insulating behavior below room temperature [8]. The slightly larger activation energy for $M=\text{Zn}$ than that for $M=\text{Ni}$ may arise from the suppression of an electron transfer of the d -electrons, owing to the presence of the non-magnetic closed-shell Zn^{2+} ion.

It should be noted that the $P2_1/n$ structure observed from XRD is centrosymmetric. Thus, a displacement of cation and anion pairs, which is the origin of many ferroelectric materials ever known, seems not to be applicable to an explanation for the large dielectric constants in Fig. 3. Recently, we found that the lanthanide-iron oxides $R\text{Fe}_2\text{O}_4$ ($R=\text{Ho-Lu}$) are the

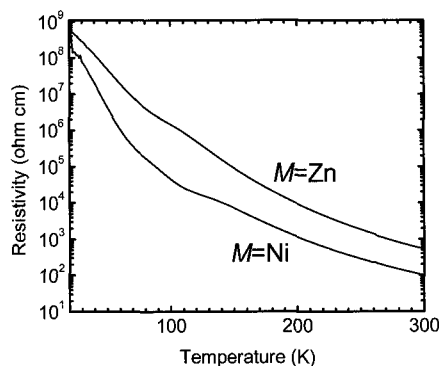


Fig. 4. Temperature dependence of AC resistivity calculated from the imaginary part of the AC dielectric response for $M=\text{Ni}$ and $M=\text{Zn}$.

ferroelectrics by the charge-ordered alignment of the Fe^{2+} and Fe^{3+} ions below 330 K [14,15]; this ferroelectricity is not accompanied by the displacement of cations and anions. A similar mechanism would be possible in the present system, taking into account that La_2MRuO_6 has the small ionic disordering of M^{2+} and Ru^{4+} (Table 1), which may break the inversion symmetry. This seems to be an analogous situation to the real-space non-symmetric ordering of Fe^{2+} and Fe^{3+} in $R\text{Fe}_2\text{O}_4$. However, more precise determination of the crystal structure should be done.

The larger dielectric constants for $M=\text{Co}$ and Ni than those for $M=\text{Mg}$ and Zn may be related to the electron transfer between the M^{2+}/Ru^{4+} ions. From the $\tan\delta$ component of the dielectric response, we have calculated the energies required for a flip of the directions of the polar regions [14]. The calculated values of ~ 0.1 - 0.2 eV (not shown) are comparable to those of the electronically ferroelectric $R\text{Fe}_2\text{O}_4$ [14,15], in which the directions of the polar regions are rotated by an electron transfer between the Fe ions. This result strongly suggests an important role of the electron transfer in the dielectric response of La_2MRuO_6 . The rotation of the polar regions is assumed to become easier with decreasing the electron-transfer energy, which manifest itself as the resistivity in Fig. 4. It is also noteworthy that a large dielectric response is observed if the polar regions have a smooth response in accordance with the AC electric field. Thus, the dielectric constant becomes larger for $M=\text{Co}$ and Ni than for $M=\text{Mg}$ and Zn .

Concerning the large α values in Fig. 3, an analogous result was also obtained for TmFeCuO_4 ($\alpha\sim 0.3$) [16], in which Fe is partially substituted by Cu in an electronically ferroelectric oxide TmFe_2O_4 ($\alpha\sim 0.1$) [15,16]. From the magnetic study on isostructural LuMgFeO_4 , the large α is rooted in a spatial randomness of the electron transfer between the Fe ions, originating from a random substitution of the non-magnetic Mg^{2+} ion at the Fe site [17]. This result suggests that the large α of La_2MRuO_6 is also ascribed to some kinds of randomness. In this context, a possible origin of the randomness may be oxygen nonstoichiometry of $\delta\sim 0.06$ in $\text{La}_2MRuO_{6+\delta}$ [10]. In addition, Table 1 indicates that the random occupation of the M and Ru ions is another possibility for the large α values.

The properties of R_2MRuO_6 with heavier R elements are also being investigated. Figure 5 shows the XRD patterns for $\text{Nd}_2\text{NiRuO}_6$. The Rietveld analysis confirmed the monoclinic $P2_1/n$ structure [3]. From the fitting parameters, an enhancement of lattice distortion was observed. As has been elucidated from many studies of perovskites, this enhancement is owing to the replacement of the smaller R^{3+} ions at the so-called A -site in the perovskite structure. For $R_2\text{NiRuO}_6$, an average Ni/Ru-O-Ni/Ru angle was estimated to be $\sim 154^\circ$ for $R=\text{La}$, $\sim 150^\circ$ for Pr and $\sim 148^\circ$ for Nd .

Figure 6 shows the magnetization plotted against the temperature for $\text{Nd}_2\text{NiRuO}_6$. Deviations between FC and ZFC curves at ~ 40 K mean the existence of magnetic irreversibility. The magnetic transition temperature was determined by a temperature derivative of each magnetization curve. The temperature was calculated to be ~ 35 K. For $\text{Pr}_2\text{NiRuO}_6$, the transition temperature was ~ 25 K. The negative Weiss temperatures of ~ -50 K

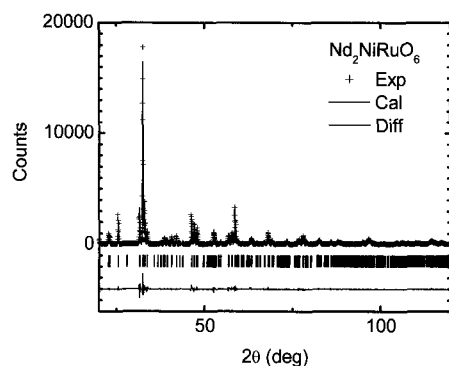


Fig. 5. XRD patterns of Nd_2NiRuO_6 ($a=5.4303(5)$, $b=5.6792(5)$, $c=7.7328(7)$ Å, $R_{WP}=13.42\%$, $R_I=2.40\%$). The experimental and the calculated patterns are labeled as Exp and Cal, respectively. The vertical lines and the lowest line stand for the calculated Bragg angles and the difference between the experimental and calculated patterns, respectively.

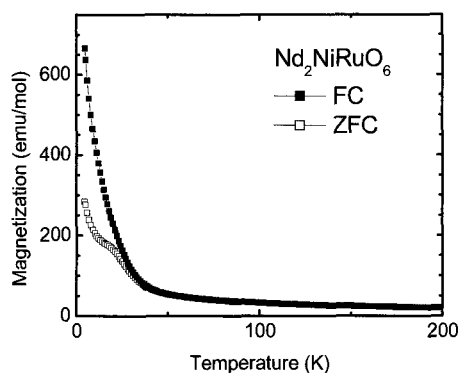


Fig. 6. Magnetization plotted against temperature for Nd_2NiRuO_6 , measured with the applied field of 1000 Oe. The transition temperature was estimated to be ~ 35 K.

for both oxides mean that the ordering is antiferromagnetic. The narrowing of the Ni/Ru-O-Ni/Ru angle reduces the magnetic interactions between the Ni/Ru ions. However, the obtained transition temperatures are not in accord with the change of the interactions. As the Pr^{3+} and Nd^{3+} ions have localized magnetic moments, one possible origin of this behavior is a contribution of the magnetic interactions between the R and Ru/Ni ions. The importance of such an interaction was suggested for quasi-one-dimensional ruthenates R_2RuO_5 [18], in which the magnetic ordering temperature has no correlation with the ionic radius of R^{3+} . To obtain further information on these oxides, their dielectric properties are currently investigated.

4. SUMMARY

Magnetic and dielectric properties of the ruthenium double perovskites R_2MRuO_6 were studied ($R=La, Pr$ and $Nd, M=Mg, Co, Ni$ and Zn). For $R=La$, the materials with the magnetic M^{2+} ions ($M=Co$ and Ni) showed magnetic ordering and large dielectric constants (~ 5000). On the other hand, for the non-magnetic M^{2+} ions ($M=Mg$ and Zn), magnetic ordering was not observed. In addition, their dielectric constants were found to be small ($\sim 100-200$). Together with the imaginary part and the $\tan\delta$ component of the dielectric response, the large dielectric constants for $M=Co$ and Ni may be related to a smooth response of polar regions. As the magnetic properties of R_2MRuO_6 with $R=Pr$ and Nd could not be understood in connection with the narrowing of the M/Ru angle, the origin of this behavior should be clarified in the future.

ACKNOWLEDGMENT

This work is partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (C).

REFERENCES

- [1] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz and F. Lichtenberg, *Nature*, **372**, 532-534 (1994).
- [2] I. Fernandez, R. Greatrex and N. N. Greenwood, *J. Solid State Chem.* **32**, 97-104 (1980).
- [3] P. A. Seinan, F. P. F. Van Berkel, W. A. Green and D. J. W. Ijdo, *Mater. Res. Bull.* **22**, 535-542 (1987).
- [4] J.-H. Choy, J.-Y. Kim, S.-H. Hwang, S.-J. Kim and G. Demazeau, *Int. J. Inorg. Mater.* **2**, 61-70 (2000).
- [5] K. Yoshii, H. Abe, M. Mizumaki, H. Tanida and N. Kawamura, *J. Alloys Compd.* **348**, 236-240 (2003).
- [6] M. Gateshki, J. M. Igartua and Y. Brouard, *Mater. Res. Bull.* **38**, 1661-1668 (2003).
- [7] R. I. Dass, J. -Q. Yan and J. B. Goodenough, *Phys. Rev.* **B69**, 094416 (2004).
- [8] For a recent review, D. I. Khomskii, *J. Magn. Magn. Mater.* **306**, 1-8 (2006).
- [9] F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **321-324**, 198 (2000).
- [10] K. Yoshii, N. Ikeda and M. Mizumaki, *Phys. Stat. Sol. (a)*, **203**, 2812-2817 (2006).
- [11] M. Mizumaki, K. Yoshii, Y. Hinatsu, Y. Doi and T. Uruga, *Phys. Scr.* **T115**, 513-515 (2004).
- [12] R. D. Shannon, *Acta Cryst.* **A32**, 751-767 (1976).
- [13] N. Ikeda, H. Kito, J. Akimitsu, K. Kohn and K. Siratori, *J. Phys. Soc. Jpn.* **63**, 4556-4564 (1994).
- [14] N. Ikeda *et al.*, *Nature*, **436**, 1136-1138 (2005).
- [15] K. Yoshii, N. Ikeda and A. Nakamura, *Physica B*, **378-380**, 585-586 (2006).
- [16] K. Yoshii, N. Ikeda and S. Mori, *J. Magn. Magn. Mater.* (2007) in press.
- [17] N. Ikeda, K. Kohn, E. Himoto and M. Tanaka, *J. Phys. Soc. Jpn.* **64**, 4371-4377 (1995).
- [18] G. Cao, S. McCall, Z. X. Zhou, C. S. Alexander, J. E. Crow and R. P. Guertin, *J. Magn. Magn. Mater.* **226-230**, 218-220 (2001)

(Received January 4, 2007; Accepted January 4, 2007)