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Structure, magnetism and transport properties of $Ce_{1x}TiO_3$

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Structure, magnetism, and transport properties were investigated for the lanthanide deficit perovskite $Ce_{1x}TiO_3$ ($0 \le x \le 0.1$). The crystal structures were found to be the orthorhombic perovskite type (*Pnma*; GdFeO₃ type). The end compound CeTiO₃ is a Mott-Hubbard type insulator, and exhibited a two-step magnetic transition at $T_N=122$ K and $T'_N\sim60$ K. It was observed that the ordering temperature T_N and ordered magnetization below T_N decreased monotonously with increasing x. Finally, magnetic order almost disappeared at x=0.1. Resistivity-temperature (ρ -T) curves revealed that the system changes to a paramagnetic metal from a magnetic insulator between x=0 and 0.05. Magnetization-field (*M-H*) curves showed the shrinkage of hysteresis loops with increasing x, leading to a paramagnetic profile at x=0.1. The results are compared with those of $Ln_{1x}TiO_3$ with Ln=La, Pr, Nd and Sm. Key words: perovskite, titanate, lanthanide deficit, insulator-metal transition

1. INTRODUCTION

The cerium titanate CeTiO₃ has an orthorhombic perovskite structure (Pnma; GdFeO₃ type) [1-2]. Because of strong Coulomb interactions between Ti3d electrons, it is regarded as a Mott-Hubbard type insulator, having a localized Ti³⁺ moment (Ti3d¹; S=1/2) on each Ti site [2]. The moments exhibit cantedantiferromagnetic order with a Néel temperature $(T_{\rm N})$ of 116-125 K.

These features are qualitatively the same as those for $LnTiO_3$ systems (Ln=La, Pr, Nd and Sm) [3-8], whose T_N varies between ~140 K (LaTiO_3) and ~50 K (SmTiO_3). They can accommodate Lndeficits up to ~33% at which total Ti³⁺ ions (Ti3d¹) for x=0 are converted to Ti⁴⁺ (Ti3d⁰) [3, 4, 6-8]. By introducing the deficit of ~10% (Ti^{3.3+}; 3d^{0.7}), the canted-antiferromagnetism disappears in all the systems, while the GdFeO₃ structure is maintained. Electrical resistivity data of La_{1-x}TiO₃ [3, 4] and Pr_{1-x}TiO₃ [8] elucidate that each system changes to a Pauli-paramagnetic metal from a magnetic insulator at x~0.1. This behavior is analogous to the insulator-metal transition in solid solutions La₁. $_{x}$ Sr_xTiO₃ [9] and Ce_{1-x}A_xTiO₃ (A=Sr and Ba) [2].

For other lanthanide titanates, properties of their lanthanide deficit phases have not been reported so far. In this work, we have investigated structural, magnetic and electrical properties for the Ce deficit system $Ce_{1-x}TiO_3$. The results are compared with the those of the above $Ln_{1-x}TiO_3$ systems.

2. EXPERIMENTAL

The samples were prepared by the ceramic method using CeO_2 (4N), TiO (3N) and Ti₂O₃ (3N), according to the reaction:

$$(1-x) \operatorname{CeO}_2 + (1-4x) \operatorname{TiO} + 2x \operatorname{Ti}_2 \operatorname{O}_3 \rightarrow \operatorname{Ce}_{1-x} \operatorname{TiO}_3$$

(x=0, 0.025, 0.05, 0.0625, 0.075 and 0.1). The initial mixtures were thoroughly ground, pelletized and fired at 1550°C for 24 hrs in vacuum of ~10⁻⁵ Pa. The firing was repeated for two or three times. The oxygen contents were determined by the TGA (thermogravimetric analysis) method. The actual oxygen contents (δ) in Ce_{1-x}TiO₃₊₆ were calculated as 0.03-0.04, indicating slight oxidation of the Ti ions during the firing [10].

The crystal structures were determined from

powder XRD (X-ray diffraction) measurements using CuK α radiation (Mac Science Co., M03XHF). The XRD patterns were refined by the Rietveld method using the program RIETAN [11]. DC magnetization measurements were carried out by a SQUID magnetometer (Quantum Design MPMS). Susceptibility-temperature (χ -T) curves were measured with an applied field (H) of 100 Oe between 4.5 and 300 K. Magnetization-field (M-H) curves were measured between ±50,000 Oe at 4.5 K. Electrical resistivity-temperature (ρ -T) curves were measured by the DC four probe method between 4.2 and 300 K. Other details have been given elsewhere [10].

3. RESULTS AND DISCUSSION

Figure 1 shows the lattice parameters obtained for all the systems. The XRD patterns consisted only of the reaction products, and were commonly refined to the orthorhombic perovskite structure (space group *Pnma*) as in the systems noted in section 1. Reliability factors were 10-12%.

The lattice parameters of CeTiO₃ were confirmed to be close to those reported previously [1, 2]. The lattice parameters tend to decrease with increasing the Ce deficit (x), as is the case for La_{1-x}TiO₃ [3] and Pr_{1-x}TiO₃ [8]. The different behavior was found for Nd_{1-x}TiO₃ [6] and Sm_{1-x}TiO₃ [7]. Namely, the *b*-length for the former system is almost independent of x, and that for the latter



Fig. 1 Lattice parameters plotted as a function of the Ce deficit (x).



Fig. 2 χ -*T* curves for Ce_{1-x}TiO₃ with (a) $x \le 0.05$ and (b) x > 0.0625.

system slightly increases with increasing x. From the present data, it was found that the unit cell volume decreased almost linearly with x from 246.65 (x=0) to 241.44 (x=0.1) Å³. This is a common feature for all the $Ln_{1-x}TiO_3$ systems quoted above, and is qualitatively explained in terms of the combined effect of the missing of the large Ln ions and the shrinkage of the Ti ions caused by the oxidation from Ti³⁺ to Ti^{3.3+}.

Figure 2(a) and (b) show the χ -T curves measured in a residual magnetization mode on heating the samples after *M*-*H* curve measurements at 4.5 K. The curve of CeTiO₃ with T_N =122 K quite resembles those reported in the previous studies, where the canted-antiferromagnetic order occurs at T_N =116-125 K [1, 2]. The inflection at T'_N ~60 K is brought about by the induced order of the Ce³⁺ moments [1].

The profile of the curve for x=0.025 ($T_N \sim 95$ K) is similar to that of CeTiO₃. This result means that the canted-antiferromagnetic order well remains at x=0.025, though magnetic interactions between Ti³⁺ are weakened by the slight change of the Ti valence. The profile of the x=0.05 curve fairly

differs from that of CeTiO₃, revealing the considerable alternation of the cantedantiferromagnetism. It is apparent that ordered magnetization below T_N drastically decreases as x is increased in the region of $x \ge 0.05$. The value of $T_{\rm N}$ also monotonously decreases with increasing x. Though the trace of the magnetic order still remains which was found from nonlinear profiles of inverse susceptibility-temperature $(1/\chi - T)$ curves below ~50 K, the order almost disappears at x=0.075 and 0.1. Therefore the change of the average Ti valence from 3+ (CeTiO₃) to 3.3+ $(Ce_{0.9}TiO_3)$ leads to the drastic collapse of the canted-antiferromagnetism. The curves for x=0.075and 0.1 are nearly the same, which implies that almost only the contribution of the free Ce³⁺ moments exists for $x \ge 0.75$.

Qualitatively, the same phenomena are observed for Ln_{1-x} TiO₃ with Ln=La, Pr, Nd and Sm. They exhibit also a systematic trend with the ionic radii of Ln^{3+} . Nd_{1-x}TiO₃ and Sm_{1-x}TiO₃ with x=0.05 show larger magnetization below T_N than that of the end compounds, while the profiles of χ -T curves are similar to those of the end compounds, and T_N monotonously decreases with increasing x [6, 7]. Also Pr_{0.95}TiO₃ shows an analogous profile of a χ -T curve to that of PrTiO₃ [8]. These results indicate that the canted-antiferromagnetism well remains at x=0.05 in $Ln_{1,r}$ TiO₃ (Ln=Pr, Nd and Sm), which might be explained in connection with the larger orthorhombic distortion than that in Ce₁ $_{x}$ TiO₃, due to the smaller ionic radii of Ln^{3+} . Namely, stronger localization of Ti3d electrons in former the systems. Thus superexchange interactions between the Ti³⁺ moments well remains even at the same deficit.

Inverse susceptibility-temperature $(1/\chi-T)$ curves derived from Fig. 2 were generally expressed in terms of the Curie-Weiss (*CW*) law above T_N . For CeTiO₃, the data was well fitted with an effective moment μ equal to a free Ce³⁺ moment (2.56 μ_B). An antiferromagnetic Weiss temperature θ ~-53 K is close to the previous result [2]. The effects from Ti³⁺ were not clearly seen probably because of the slight oxygen nonstoichiometry as discussed elsewhere [10]. Both the values of μ and θ did not change much with x.



Fig. 3 *M-H* curves at 4.5 K for $Ce_{1-x}TiO_3$ with (a) x=0 and (b) x=0.05 and 0.1.

Figure 3 shows the *M*-*H* curves at 4.5 K for x=0, 0.05 and 0.1. The curve for x=0 (CeTiO₃) exhibits a large hysteresis loop with saturation magnetization. The coercivity is 4,000-5,000 Oe. Though the curve of x=0.05 (Ce_{0.9}TiO₃) exhibits a hysteresis loop, magnetization attains no saturation up to 50,000 Oe. From the result in Fig. 2, this is apparently due to the increasing paramagnetic component. On the other hand, for Pr_{0.95}TiO₃, a large hysteresis loop was observed with the coercivity of 25,000-30,000 Oe [8]. The curve of x=0.1 is almost paramagnetic, as in Fig. 2(b).

Figure 4 shows the ρ -T curves for x=0, 0.05 and 0.1 systems. The semiconductive curve of CeTiO₃ (x=0) provided a band gap of ~80 meV above T_N , which is about ten times larger than that in the previous study [2]. This value was the same for two samples studied in the present work. A possible origin of this difference is different oxygen nonstoichiometry (δ), i.e., ~0 in Ref. 2 and 0.3-0.4 in this work. However, oxygen nonstoichiometry leads to metallic properties as found for LaTiO₃ [9]. Further studies are needed for elucidating this discrepancy. The gap decreases below T_N down to ~40 meV, which is a similar



Fig. 4 ρ -T curves for Ce_{1-x}TiO₃ with (a) x=0 and (b) x=0.05 and 0.1.

tendency to that for $PrTiO_3$ [5, 8].

 $Ce_{0.95}TiO_3$ (x=0.05) shows metallic behavior above T_N . Thus an insulator-metal (*IM*) transition occurs between x=0 and 0.05. For $Pr_{1-x}TiO_3$, the curve with x=0.05 is still weakly semiconductive [8], indicating an *IM* transition between x=0.05 and 0.1. This difference is qualitatively consistent with the different degree of localization of Ti3d between these systems discussed above. Below T_N , the resistivity shows a clear upturn because of the remaining canted-antiferromagnetism. The curve exhibits also a characteristic plateau above 250 K. Similar phenomena were observed also for metallic $Pr_{0.9}TiO_3$, semiconductive $Pr_{0.95}TiO_3$ [8], and semiconductor-like $La_{1-x}TiO_3$ (x~0.04) [4].

 $Ce_{0.9}TiO_3$ (x=0.1) shows a more flattened metallic profile of the ρ -T curve with slight increase of resistivity below T_N . $Pr_{0.9}TiO_3$ exhibited slight decrease of resistivity below T_N [8]. This increase reflects the existence of the cantedantiferromagnetism even at x=0.1 as noted earlier. Further studies with larger x values are in progress, and will be published in the near future.

were investigated for Ce_{1-x}TiO₃ ($0 \le x \le 0.1$). The crystal structures were the orthorhombic perovskite type (GdFeO₃ type). CeTiO₃ exhibited a two-step magnetic transition at $T_N=122$ K and $T'_N\sim 60$ K. The ordering temperature T_N and ordered magnetization below T_N decreased monotonously with increasing x. Finally, magnetic order almost disappeared at x=0.1. M-H curves showed the shrinkage of hysteresis loops with increasing x, leading to a paramagnetic profile at x=0.1. ρ -T curves revealed that the system changes to a paramagnetic metal from a magnetic insulator between x=0 and 0.05.

REFERENCES

- J. P. Goral and J. E. Greedan, J. Mag. Mag. Mater., 37, 315-321 (1983), and references therein.
- [2] J. E. Sunstrom VI, S. M. Kauzlarich and M. R. Antonio, Chem. Mater., 5, 182-191 (1993).
- [3] M. J. MacEachern, H. Dabkowska, J. D. Garrett, G. Amow, W. Gong, G. Liu and J. E. Greedan, *Chem. Mater.*, 6, 2092-2102 (1994).
- [4] D. A. Crandles, T. Timusk, J. D. Garrett and J. E. Greedan, *Phys. Rev.* B49, 16207-16213 (1994).
- [5] D. A. MacLean, K. Seto and J. E. Greedan, J. Solid State Chem., 40, 241-247 (1981).
- [6] G. Amow and J. E. Greedan, J. Solid State Chem., 121, 443-450 (1996).
- [7] G. Amow, J. E. Greedan and C. Ritter, J. Solid State Chem., 141, 262-269 (1998).
- [8] K. Yoshii, A. Nakamura and H. Abe, at 12th International Conference on Ternary and Multinary Compounds, Taiwan (2000).
- [9] Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima,
 T. Arima, K. Kumagai and Y. Iye, *Phys. Rev.* Lett., **70**, 2126-2129 (1993).
- [10] K. Yoshii, A. Nakamura and H. Abe, J. Alloys Comp., 290, 236-243 (1999).
- [11] F. Izumi "The Rietveld method", Ed. by R. A.
 Young, Oxford Univ. Press, Oxford, (1993)
 pp. 121-124; Y. -I. Kim and F. Izumi, J.
 Ceram. Soc. Jpn., 102, 401-404 (1994).

4. SUMMARY

Structure, magnetism, and transport properties