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LETTER TO THE EDITOR

Magnetic and Structural Studies of $La_{1-x}Sm_xTiO_3$ ($0 \leq x \leq 1$)

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It was found that $La_{1-x}Sm_xTiO_3$ ($x = 0$, 0.0625, 0.1875, 0.25, 0.375, 0.5, 0.75, and 1) systems form a complete solid solution phase with the orthorhombic perovskite structure ($GdFeO_3$ type). Between $x = 0$ ($LaTiO_3$; T_N (Néel temperature) ~ 130 K) and $x = 1$ ($SmTiO_3$; $T_N \sim 50$ K), the susceptibility-temperature (χ–T) curves exhibited a characteristic peak phenomenon below T_N's only for $0.0625 \leq x \leq 0.375$. Such behavior almost disappears for $x \geq 0.5$.

Orthorhombic $LaTiO_3$ is reported to be a so-called canted antiferromagnet with T_N (Néel temperature) ~ 140 K (1–5). The system loses magnetic ordering and changes into a paramagnetic metal by slight oxidation of the Ti ions, caused by nonstoichiometry of the oxygen content (3) by substitution of La^{3+} for Sr^{2+} ions ($La_{1-x}Sr_xTiO_3$) (3, 4), or by a slight La deficiency (5, 6). As a different approach to this system, in the present work, we prepared a solid solution of $La_{1-x}Sm_xTiO_3$ ($0 \leq x \leq 1$) to elucidate the effects of lanthanide substitution on its structural and magnetic properties. We found a characteristic peak phenomenon in the magnetization–temperature curves in some La-rich compounds. This paper briefly reports the results.

Samples were prepared by the conventional ceramic method:

$$\frac{(1-x)}{2}La_2O_3 + \frac{x}{2}Sm_2O_3 + \frac{1}{2}Ti_2O_3 \rightarrow La_{1-x}Sm_xTiO_3.$$

The x values for $La_{1-x}Sm_xTiO_3$ were 0.0625, 0.1875, 0.25, 0.375, 0.5, 0.75, and 1.0. Starting materials were dried La_2O_3 (99.99%) and Sm_2O_3 (99.99%) and as-cast Ti_2O_3 (99.9%) (Soekawa Chemical). The reaction mixtures (~ 2 g) were thoroughly ground, pelletized, and fired in a tungsten crucible at 1550°C for 24 h in a vacuum better than 10^{-5} Torr. The firing was repeated two to three times, with intermediate grinding. The samples were gray–black in color. Some of the samples were prepared twice in a separate run, and were verified to show reproducibility in structural and magnetic properties. They were examined by the powder XRD (X-ray diffraction) method using Cu$K\alpha$ radiation (Rigaku Geigerflex). The lattice parameters were calculated from least-squares fitting.

The oxygen content y in $La_{1-x}Sm_xTiO_y$ was determined in a TGA (thermogravimetric analysis) apparatus from the weight gain of the samples when oxidized in air at 1000°C. The y value determined was 3.02 ± 0.02 for each sample. For convenience, we designate the system hereafter as $La_xSm_{1-x}TiO_3$.

DC magnetization measurements were made using a SQUID magnetometer (Quantum Design MPMS). Susceptibility–temperature (χ–T) curves for each sample were measured under both the FC (field-cooled) and ZFC (zero-field-cooled) conditions. The former was measured on cooling from 300 to 4.5 K at 100 G. The latter was measured in a residual magnetization mode on heating the sample to 300 K after zero-field cooling to 4.5 K, applying a 55,000 G field, and then reducing it to 100 G. Magnetization–magnetic field (M–H) isotherm curves were measured at several temperatures with changing field between $\pm$ 55,000 G.

Lattice parameters obtained from the XRD measurements are plotted in Fig. 1 for all of the samples as a function of Sm content (x) in $La_{1-x}Sm_xTiO_3$. All of the diffraction peaks originated only from the reaction products, and could be suitably assigned to the single-phase orthorhombic perovskite structure ($GdFeO_3$ type). The lattice parameters for $LaTiO_3$ ($x = 0$) and $SmTiO_3$ ($x = 1$) obtained here are in fair agreement with those of previous studies (2, 6–8). In Ref. (2), they are $a = 5.601$ Å, $b = 5.590$ Å, $c = 7.906$ Å, $V = 247.5$ Å^3 for $LaTiO_3$ and $a = 5.660$ Å, $b = 5.454$ Å, $c = 7.732$ Å, $V = 238.4$ Å^3 for $SmTiO_3$. It is seen that the b and c lengths and cell volume (V) decrease almost continuously with x, obviously owing to the lanthanide contraction. The length of the a axis increases with increasing x up to that of $SmTiO_3$ ($x = 1$).

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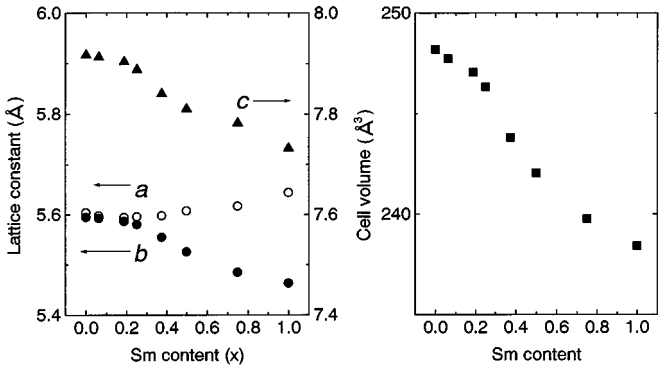

FIG. 1. Lattice parameters plotted against Sm content (x) for $La_{1-x}Sm_xTiO_3$.

The composition dependence of all of the lattice parameters changes at $x \sim 0.3$. The changes are rather gradual for $x < 0.3$, but become somewhat steeper for $x > 0.3$. Thus, it is speculated that crystallographically the system with $x < 0.3$ is closely similar to $LaTiO_3$ ($x = 0$) with slight modification, but tends increasingly to resemble $SmTiO_3$ ($x = 1$) with $x > 0.3$. The magnetization peak phenomenon was essentially distinctly observed only for $x < 0.3$, as discussed below.

Figure 2 shows χ–T curves for the end compounds $LaTiO_3$ and $SmTiO_3$ and for the solid solution $La_{0.9375}Sm_{0.0625}TiO_3$, where the substitution is least (6.25%) in the present work. Only the ZFC curves are shown for $LaTiO_3$ and $SmTiO_3$, for they were nearly identical to the FC curves. The χ–T curve of $LaTiO_3$ resembles those previously reported (3). This compound is called a canted antiferromagnet with T_N (Néel temperature) $\sim$140 K. The present T_N value is somewhat lower, $\sim$130 K, probably because of the slight oxidation (3). However, the magnetic moment at 4.5 K ($\sim 9.2 \times 10^{-3}$ μ_B/Ti ion) is close to that in Ref. (3) ($\sim 1.0 \times 10^{-2}$ μ_B/Ti ion). As far as the authors know, no detailed magnetic properties of $SmTiO_3$ have been reported. The compound showed a transition at $\sim$50 K (also called T_N for convenience). The M–H curve at 4.5 K indicates that the compound is nearly paramagnetic, with a small residual moment ($\sim 7.9 \times 10^{-4}$ μ_B/molecule).

The χ–T curves of the mixed compound $La_{0.9375}Sm_{0.625}TiO_3$ are entirely different. As the temperature is lowered from 300 K in the FC run, the sample first exhibits a transition at $\sim$110 K. This temperature is tentatively also labeled T_N. With further decrease of the temperature, the susceptibility exhibits a characteristic broad peak at $\sim$60 K (peak temperature, defined as T_P), and finally decreases at $\sim$10 K down to $\sim 10^{-4}$ emu/g. In the ZFC run, a similar susceptibility peak is observed as well. However, the maximum susceptibility at T_P (χ_{max}) is much less and T_P itself is quite different, $\sim$25 K.

A similar peak phenomenon in the χ–T curve was consistently observed for $x \leq 0.375$. This is seen in Fig. 3, which shows the FC χ–T curves for several representative samples. Each ZFC curve for $x \neq 0.9375$ having the peak phenomenon exhibited a profile similar to the corresponding FC curve with much lower χ_{max}. The $x = 0.375$ curve is omitted in the figure, for the features mentioned above can be hardly recognized at this ordinate scale. The values T_N, T_P, and χ_{max} change with Sm content (x). With x increasing from 0.0625 to 0.375, T_N shows a tendency to decrease from $\sim$110 to $\sim$80 K, whereas T_P increases from $\sim$60 to $\sim$80 K, accompanying the reduction in χ_{max}. The peak in the χ–T curve almost vanishes for $x \geq 0.5$, probably through the crossing of T_N nd T_P around 80 K. It is therefore inferred that the slight modification of the canted spin ordering in $LaTiO_3$ is brought about by the Sm substitution, leading to the onset of the characteristic peak phenomenon in this system. In fact, this phenomenon is almost confined to the region $x < 0.3$, where the change of the lattice parameters from those of $LaTiO_3$ is rather small (Fig. 1).

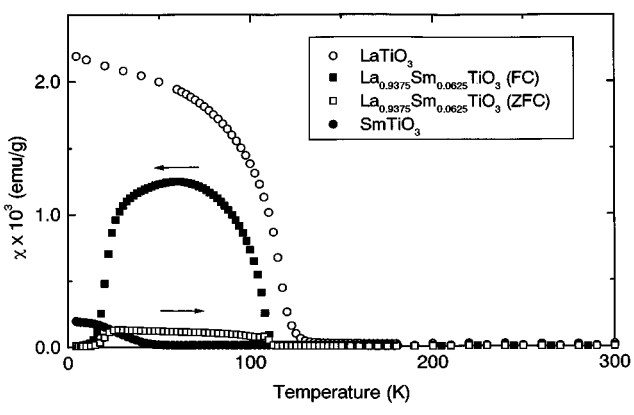

FIG. 2. χ–T curves for $LaTiO_3$, $SmTiO_3$, and $La_{0.9375}Sm_{0.0625}TiO_3$.

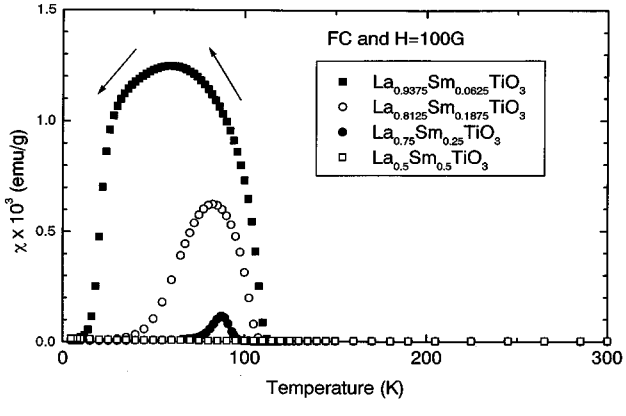

FIG. 3. The FC χ–T curves for samples other than $LaTiO_3$ and $SmTiO_3$.

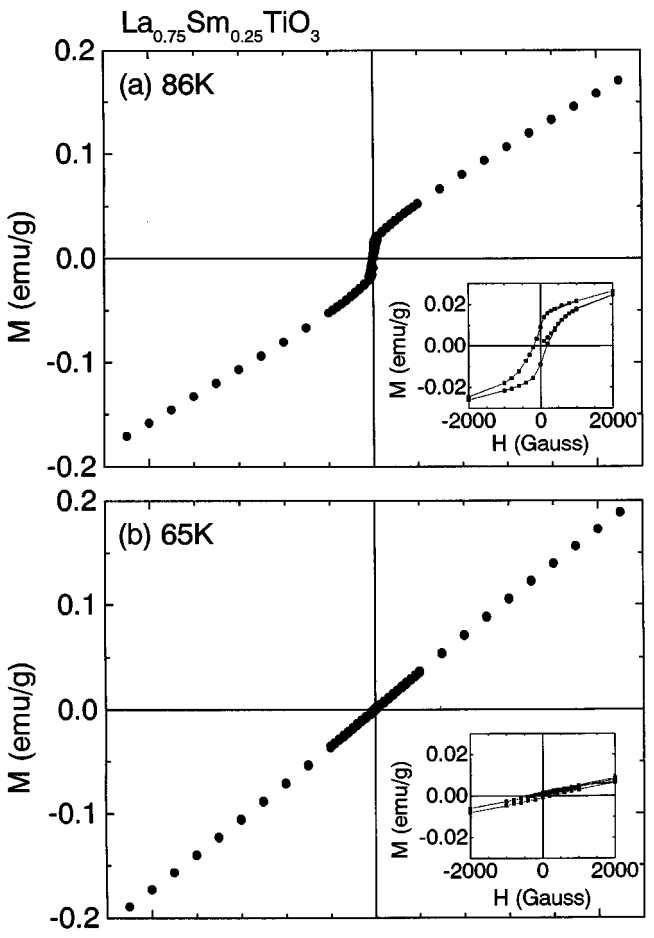

FIG. 4. *M–H* curves measured at (a) 86 K and (b) 65 K for $La_{0.75}Sm_{0.25}TiO_3$.

Figure 4 shows the *M–H* curve of $La_{0.75}Sm_{0.25}TiO_3$ measured at 85 K (T_P) and 65 K. Close to T_P, residual magnetization is clearly observed, whereas it is quite small at 65 K. At lower temperatures, it was found that the residual magnetization gradually increased, however, was much lower than those at T_P. For all the samples exhibiting the peak phenomenon, similar behavior of the *M–H* curves was observed below T_N.

In summary, we found that a solid solution system $La_xSm_{1-x}TiO_3$ ($x = 0$, 0.0625, 0.1875, 0.25, 0.375, 0.5, 0.75, and 1.0) formed an orthorhombic perovskite phase. Between $x = 0$ ($LaTiO_3$; $T_N \sim 130$ K) and $x = 1$ ($SmTiO_3$; $T_N \sim 50$ K), a characteristic magnetization peak phenomenon was clearly observed only for $x < 0.3$ where the crystallographic alteration from $LaTiO_3$ is rather minor.

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