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Magnetic properties of $(Dy_xLa_{1-x})_2Ti_2O_7$

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In our paper we focus on magnetic properties of $(Dy_xLa_{1-x})_2Ti_2O_7$ system, which may combine ferroelectric properties of $La_2Ti_2O_7$ with magnetic structure and ferroelectricity of spin frustrated system of $Dy_2Ti_2O_7$. Despite of the fact that SEM indicates homogeneous samples with expected chemical composition, XRPD measurements revealed the limited solubility of La or Dy dopant in parent compounds, and coexistence of two crystal structures — pyrochlore cubic $Fd\bar{3}m$ and orthorhombic $Pna2_1$ in intermediate concentration range between $x = 0.68$ and $x = 0.32$. The substitution of Dy by La expands the crystal lattice of both crystal structures. The AC susceptibility measurements revealed that spin freezing temperature T_f shifts to higher temperature with La substitution and provided an evidence either of new magnetic phase with $Pna2_1$ crystal structure or creation of new dynamical behaviour in $Fd\bar{3}m$ phase below $x = 0.68$ in the range between T_i and T_f. The frequency and magnetic field dependences on samples with pyrochlore structure resemble features typical for $Dy_2Ti_2O_7$. The heat capacity measurements indicate that the temperature of transition to spin ice ground state at T_i is not affected by La substitution for concentration with $x \leq 0.32$.

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PACS/topics: crystal structure, ferroelectric compound, spin ice, AC susceptibility, heat capacity

1. Introduction

$La_2Ti_2O_7$ is a well known high temperature ferroelectric compound (the Curie temperature $T_C \approx 1500\,^\circ$C), which exhibits a strong piezoelectric and electro-optic effect. Moreover it has a high dielectric constant with a low temperature coefficient of capacitance and a low dielectric loss at microwave frequency. In addition, it possesses good photocatalytic activity [1–4]. $La_2Ti_2O_7$ does not form the expected isometric pyrochlore structure-type, which is typical for many of the heavy-rare earths and transition metal oxides. It rather forms a layered structure comprised of slabs of the ABO_3 perovskite structure [4], which is monoclinic, $P2_1$ at room temperature. The structure becomes orthorhombic $Cmc2_1$ at 780 °C, and at 1500 °C it transforms into the paraelectric $Cmcm$ phase. On the other hand $Dy_2Ti_2O_7$ is identified as a spin-ice material with the pyrochlore structure and crystallizes into a face centred cubic structure $Fd\bar{3}m$ [5–9]. The dynamical freezing behaviour seen in $Dy_2Ti_2O_7$ differs from the critical slowing down observed in conventional disordered spin-glass materials. Another difference between the spin freezing in $Dy_2Ti_2O_7$ and that in conventional disordered spin glasses is the magnetic field dependence. Recently, two ferroelectric transitions at $T_{C1} = 25$ K and $T_{C2} = 13$ K were observed in $Dy_2Ti_2O_7$ [10]. Remarkable magnetoelectric coupling was identified below the lower transition temperature, with significant suppression of the electric polarization on applied magnetic field. In our paper, we focus on magnetic properties of $(Dy_xLa_{1-x})_2Ti_2O_7$ system at low temperature, which may combine ferroelectric properties of $La_2Ti_2O_7$ with magnetic structure and ferroelectricity in $Dy_2Ti_2O_7$.

2. Experiment preparation

$(Dy_xLa_{1-x})_2Ti_2O_7$ crystals for $x = 0.00$, 0.15, 0.32, 0.50, 0.68, 0 85, 1.00, and $Y_2Ti_2O_7$ were grown by optical floating zone method in a four mirror furnace in the oxygen atmosphere. The presence of secondary phase and verification of chemical composition were investigated by scanning electron microscope method (SEM) on the microscope TESCAN VEGA-3LMU equipped with EDX spectrometer BRUKER X-Flash 410M. The study confirmed the expected average chemical composition and did not reveal any parasitic inclusions. The X-ray powder diffraction (XRPD) performed on powdered samples by the Rigaku Ultima IV diffractometer confirmed the expected crystal structure of parent compounds and revealed that only samples for $x = 0.00$, 0.15, 0.85, and 1, are single phase materials (Fig. 1). Lattice parameter of pyrochlore crystal structure $Fd\bar{3}m$ of $(Dy_xLa_{1-x})_2Ti_2O_7$ increases with substitution of Dy^{3+} ion by La^{3+} ion with larger ionic radius from 10.149 Å to 10.148 Å, 10.166 Å, 10.166 Å, 10.181 Å for $x = 1.00$, 0.85, 0.68, 0.5, and 0.32, respectively. The same tendency can be seen for La-rich samples which adopt $Pna2_1$ orthorhombic crystal structure. In this structure a parameter is not affected by substitution, b and c parameters increases from $a = 25.746$ Å, $b = 7.727$ Å, $c = 5.489$ Å for $x = 0.66$ to $a = 25.745$ Å, $b = 7.821$ Å, $c = 5.550$ Å for $x = 0.00$.

Our results indicate that the solubility of dopant (La or Dy) is limited, and two phases exists in the range between $x = 0.32$ and 0.68. In the case of $La_2Ti_2O_7$

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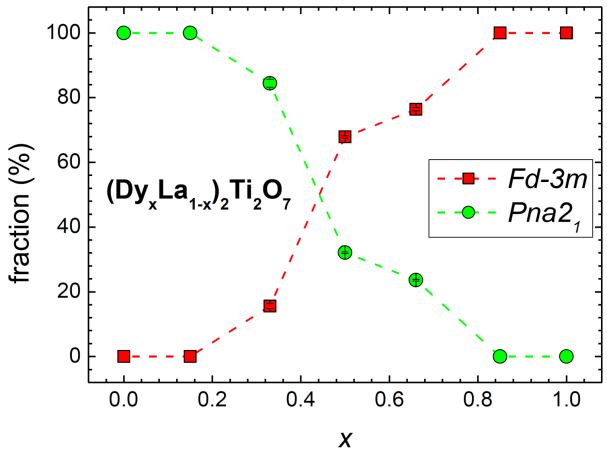

Fig. 1. The fraction of different crystal structures in samples as determined from XRPD measurements.

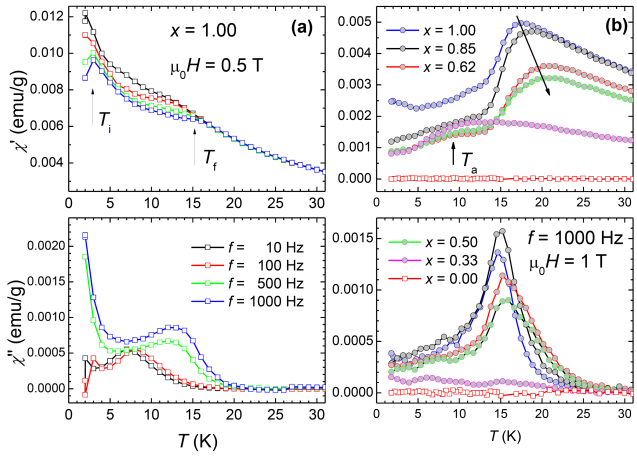

Fig. 2. Summary of AC susceptibility measurements of powdered $(Dy_xLa_{1-x})_2Ti_2O_7$ with respect to applied DC magnetic field, frequencies of driving field and chemical composition.

and La-rich samples $Pna2_1$ orthorhombic crystal structure [11] describes our XRPD data better than monoclinic $P2_1$ [1–4].

3. Magnetization and AC susceptibility results

Magnetization and AC susceptibility measurements were done by the Quantum Design MPMS XL-5 SQUID magnetometer on powdered crystals. The temperature dependence of magnetization and the absence of irreversibility in hysteresis loop indicate that $La_2Ti_2O_7$ is a diamagnetic material containing traces of magnetic impurities with magnetic phase transitions at 56 K and 10 K involving ferrimagnetic ordering. These impurities are not identical with Mott isolator $LaTiO_3$ with the Néel temperature $T_N = 146$ K [12]. The characteristic feature of the inverse susceptibility of $Dy_2Ti_2O_7$ are three temperature ranges with different slope of $1/\chi(T)$, i.e., (i) high temperature range from 360 K to 200 K yielding the Curie Weis temperature $\Theta = -44.4$ K, (ii) range from 190 K to 40 K with $\Theta = -7.7$ K, and finally (iii) range from 20 K to 2 K with $\Theta \approx 0.5$ K indicating reduction of antiferromagnetic correlations and evolution of small ferromagnetic correlations. These, in fact, have been already observed in vicinity of transition to spin ice ground state at T_i [5]. The change of the slope corresponds very well with the next highest excited state which is expected to be around 200 K [5]. Substitution of Dy^{3+} with nonmagnetic La^{3+} reduces the transition between high and low temperature regions from 150 K to 50 K and antiferromagnetic correlation from $\Theta = -40.8$ K to $\Theta = -7.3$ K for x from 0.85 to 0.32, respectively. The small ferromagnetic correlations for sample with $x = 0.85$ are suppressed and $\Theta \approx 0.2$ K.

Two distinct strongly frequency dependent maxima both in phase component χ' and out of phase component χ'' of AC susceptibility are characteristic features of $Dy_2Ti_2O_7$ (see Fig. 2a). Their different frequency dependences suggest the existence of two different types of dynamical behaviour. One of them, T_i, observed below 2 K, is related to a highly degenerate ground state — "spin ice" state and another related to spin freezing is evident at higher temperatures below $T_f \approx 10$ K [6–8]. The dynamical freezing behaviour seen in $Dy_2Ti_2O_7$ differs from the critical slowing down observed in conventional disordered spin-glass materials. In spin glasses, T_f decreases with increasing magnetic field strength, while in $Dy_2Ti_2O_7$, the opposite tendency is seen for applied magnetic fields. Our results of AC susceptibility measurements with respect to an applied DC magnetic field, frequencies of driving field and chemical composition, which are summarised in Fig. 2 confirm these basic features. The effect of different magnetic field assuming $f = 1$ kHz is demonstrated in Fig. 2a and 2b. Both the maxima at T_i and T_f are present in AC susceptibility for magnetic field of 0.5 T. The enlargement of the field to 1 T shifts the maximum at T_f to higher temperature and makes the maximum bigger. That is why we decided to study the effect of La substitution by measurements taken in magnetic field 1 T. Our measurements indicate that strong frequency dependence remains maintained on doped samples. The maximum at T_f shifts to higher temperature with La substitution and new anomaly at T_a marked by the arrow (Fig. 2b) starts to develop. Figure 2b summarises the effect of La substitution on measurements at one frequency of the driving field. The shift of T_f is evident and the anomaly at T_a provides an indication of new magnetic phase with $Pna2_1$ crystal structure and we see new dynamical behaviour in $Fd\bar{3}m$ phase below $x = 0.68$. The reduction of the maxima in AC susceptibility can be attributed to the reduced amount of cubic phase in the sample which may indicate that the feature known from the spin ice system is still strong and new dynamical behaviour develops. The increase of the volume of the elementary cell with La substitution is larger for higher concentration and stronger effect on magnetic processes can be expected.

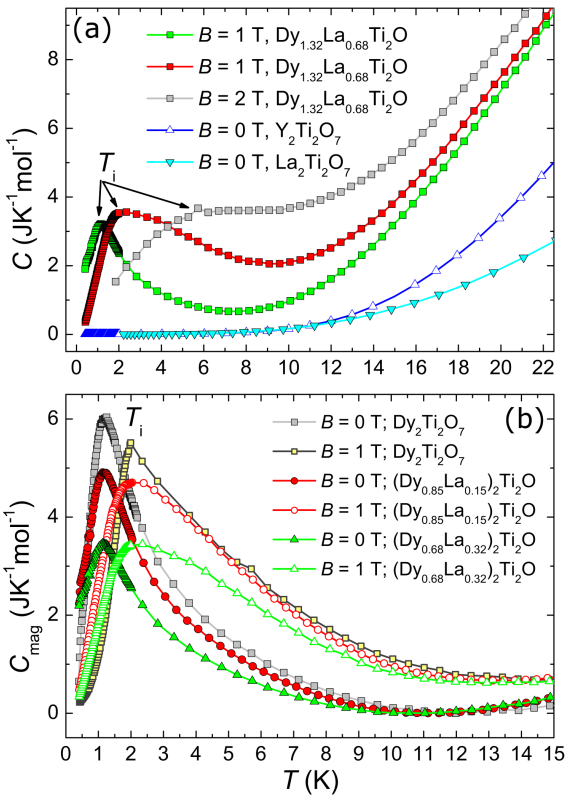

Fig. 3. Summary of heat capacity (a) comparison of field dependence for $Dy_{1.32}La_{0.68}Ti_2O_7$ and non magnetic compounds $La_2Ti_2O_7$ and $Y_2Ti_2O_7$, (b) effect of La doping on the magnetic part $C_{\rm mag}$.

4. Heat capacity results

The heat capacity measurements were performed by PPMS from Quantum Design using ^{3}He probe for measurements below 2 K. The comparison of heat capacity for $Dy_{1.32}La_{0.68}Ti_2O_7$ with heat capacity of nonmagnetic $La_2Ti_2O_7$ and $Y_2Ti_2O_7$ is shown in Fig. 3a. Our measurements confirmed the expected effect of magnetic field, which shifts the peak at T_i to higher temperatures and smears the peak slightly out. The heat capacity of $Dy_2Ti_2O_7$ consists of the magnetic contribution $C_{\rm mag}$ and the lattice contribution βT^3 with $\beta = 4.66 \times 10^{-4}$ J K^4/mol, yielding the Debye temperature $T_{\rm D}$ = 339 K. The value of β was determined from linear part of $\frac{C}{T}(T^2)$ dependence in the range 10 K–25 K, and determined $T_{\rm D}$ is comparable with already published results [9]. The magnetic contribution C_{mag} shown in Fig. 3b was obtained by subtracting the lattice contribution βT^3 from the total heat capacity C for each sample. The peak at T_i clearly shifts to higher temperature with magnetic field but the position of the peak does not change with La substitution for zero magnetic field and 1 T.

5. Conclusions

In conclusion the substitution of Dy^{3+} with La^{3+} leads to expansion of pyrochlore cubic lattice, which affects the unique spin arrangement of $Dy_2Ti_2O_7$ at low temperature by shifting the spin freezing transition at T_f to higher temperature. This leaves the transition to spin ice state at T_i unchanged for low concentrations to $x = 0.68$. AC susceptibility data revealed new anomaly at T_a below T_f which indicate new magnetic phase with crystal structure $Pna2_1$ or new dynamical behaviour in $Fd-3m$ phase in the range from $x = 0.68$ to 0.33.

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