# Magnetic entropy change of a rare earth garnet $(Gd_{0.5}Dy_{0.5})_3(Ga_{0.875}Fe_{0.125})_5O_{12}$

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**Abstract**

The working refrigerant in magnetic refrigerators has been $Gd_3Ga_5O_{12}$ (GGG) in the temperature range from 1 K to 15 K. It has been shown that substitution of Ga for Fe in GGG can make entropy change large in high temperature region. In order to increase the entropy change with small magnetic field, substitution of Gd for Dy is expected to be useful because of larger g-factor of Dy than Gd. The magnetization of $(Gd_{0.5}Dy_{0.5})_3(Ga_{0.875}Fe_{0.125})_5O_{12}$ (GDGIG) was measured and the entropy change was calculated. This compound had larger entropy change with small magnetic field than that without Dy, though the absolute entropy change at low temperatures with large applied field was smaller due to the ground state doublet of Dy.

*Key words:* magnetic refrigeration; magneto-caloric effect; magnetic material

## 1. Introduction

Magnetic refrigeration is a well-known technique to achieve below 1K on the basis of adiabatic demagnetization of a paramagnetic material. Adiabatic demagnetization refrigerators (ADR) are the oldest refrigerator of reaching milli-Kelvin temperatures. They recently attract attention for space application due to the simple electrical control and independence of gravity compared with the dilution refrigerator. When it is combined with cryocooler, an ADR can provide sub-Kelvin temperature without cryogenic liquid.

In the temperature range between 1 and 15 K, gadolinium gallium garnet, $Gd_3Ga_5O_{12}$ (GGG) has been commonly used as magnetic refrigerant[1,2]. Considering the connection between ADRs and cryocoolers, it is preferable for magnetic material to have large entropy change induced by modest applied magnetic field above 15 K.

On the basis of this requirement, gadolinium gallium iron garnet $Gd_3(Ga_{1-x}Fe_x)_5O_{12}$ (GGIG) has been studied [3,4]. The strongest exchange interaction are between Fe atoms on octahedral sites and Fe atoms on tetrahedral sites. The coupling between the Gd atoms and the Fe atoms is relatively weak[5]. For low Fe concentrations, which is low enough the percolation limit, Gd ions would be expected to form small clusters due to magnetic exchange interaction between Gd and Fe. These nanometer scale clusters might show superparamagnetism which would give large entropy change at high temperatures and lower fields. R. McMichael, et al.[4] has shown the significantly enhanced magnetic entropy change above 15 K under a field of 1 T.

We have measured the magnetization and specific heat of $Gd_3(Ga_{1-x}Fe_x)_5O_{12}$ for various x [6] and have confirmed larger entropy change at high temperatures with higher Fe concentration. The specific heat above the transition temperature under 0 T becomes larger

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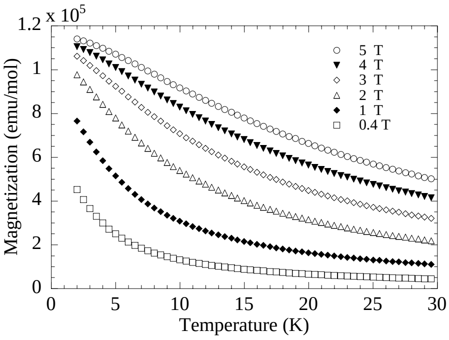


Fig. 1. Magnetization of $(Gd_{0.5}Dy_{0.5})_3(Ga_{0.875}Fe_{0.125})_5O_{12}$ as a function of temperature for 0.4, 1, 2, 3, 4 and 5 T applied field.

with the increase of Fe concentration. Then, GGIG for x = 0.125 is suitable for the Carnot cycle.

We have directed our attention to Dy atom which is known larger g-factor than Gd in garnet structure [7]. The ground state multiplet $^6H_{15/2}$ of the $Dy^{3+}$ ion is split into eight Kramer's doublets and has a large g-factor in crystal field. The large g-factor may result in large entropy change at the higher temperatures and small magnetic field.

## 2. Results and discussion

A polycrystalline $(Gd_{0.5}Dy_{0.5})_3(Ga_{0.875}Fe_{0.125})_5O_{12}$ (GDGIG) has been used for magnetization measurement using a SQUID magnetometer. The magnetization is shown in Fig. 1 as a function of temperature for 0.4, 1, 2, 3, 4 and 5 T.

The magnetocaloric effect can be related to the magnetic properties of the material through a thermodynamic Maxwell relation $\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$ . With this relation, the isothermal entropy change can be expressed as,

$$\Delta S = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'. \quad (1)$$

The entropy change, $\Delta S$ were calculated using Eq. 1 by numerical differentiation and integration of the magnetization. Figure 2 shows the entropy reduction of GDGIG for 1, 3 and 5 T. Those of GGG and GGIG (x=0.125) are also shown for comparison. In Fig. 2, the magnetic entropy change is plotted as absolute values because it is reduced by applied field so that the entropy change given by Eq. 1 is negative. The temperature dependence of the entropy reduction is similar for the three samples. In comparison between the three sample, the entropy reduction of GDGIG is the largest throughout the temperature range in

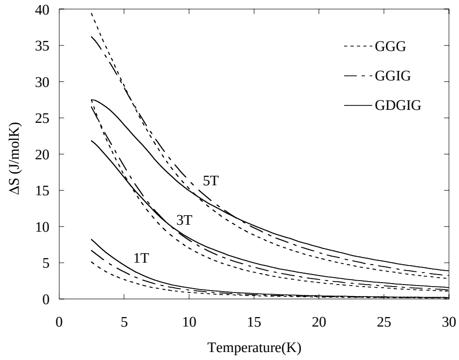


Fig. 2. entropy change of $(Gd_{0.5}Dy_{0.5})_3(Ga_{0.875}Fe_{0.125})_5O_{12}$ (GDGIG) as a function of temperature for 1, 3 and 5 T applied field. Those of GGG and GGIG (x=0.125) are also shown for comparison.

1T magnetic field, above 9 K in 3 T and above 13 K in 5 T. The substitution of Gd for Dy has enhanced the entropy change in small magnetic field and high temperature.

In the large magnetic field and low temperature, entropy reduction of gadolinium garnet is larger than that substituted for Dy atom. $Gd^{3+}$ ion has total angular momentum $J = 7/2$ so that the upper limit of $\Delta S = nk_B \ln(2J + 1)$. Although $Dy^{3+}$ has $J = 15/2$, the large crystal field produces a ground state energy level Kramer's doublet. The first ground state of $Dy^{3+}$ in gallium garnet is ∼30 K, resulting in entropy reduction, $\Delta S$ of only $nk_B \ln 2$. Then, the total entropy reduction of GDGIG has been smaller than gadolinium garnet in low temperature and high field.

Substituting Gd for Dy enhanced the entropy change of GGIG in small magnetic field and high temperature. $(Gd_{1-y}Dy_y)_3(Ga_{1-x}Fe_x)_5O_{12}$ may allow wider temperature operation of a magnetic refrigerator.

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