

Magnetocaloric effect in  $\text{La}_{0.7-x}\text{Ca}_{0.28}\text{Sr}_{0.02}\text{MnO}_3$  perovskites

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Much attention has been paid to perovskite manganese oxides  $R_{1-x}A_x\text{MnO}_3$  for the last few decades due to their colossal magnetoresistance and large magnetocaloric effect<sup>[1-5]</sup>. Until now, many studies have been made on substitution of  $\text{La}^{3+}$  by alkali metals or alkaline-earth metals<sup>[1-3]</sup>. In this work, self-doped polycrystalline  $\text{La}_{0.7-x}\text{Ca}_{0.28}\text{Sr}_{0.02}\text{MnO}_3$  perovskites were prepared and the influence of the vacancy doping level on the magnetocaloric effect was investigated.

Polycrystalline samples of  $\text{La}_{0.7-x}\text{Ca}_{0.28}\text{Sr}_{0.02}\text{MnO}_3$  ( $x=0.00-0.10$ ) were synthesized by sol-gel technique. The phase identification and structural analysis were performed on an x-ray powder diffractometer (XRD). The morphology and the particle size distribution of the samples were examined by direct observation via scanning electron microscopy (SEM). The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM).

The X-ray diffraction measurements show a clean single orthorhombic phase for the  $\text{La}_{0.7-x}\text{Ca}_{0.28}\text{Sr}_{0.02}\text{MnO}_3$  sample. The ferromagnetic ordering transition temperature  $T_c$  was found to be 227, 257, 263, 264, 268, and 270 K for  $x = 0.00, 0.02, 0.04, 0.06, 0.08,$  and  $0.10$ , respectively. The possible reason of this result is that the La site vacancy doping influences the mean manganese valance and changes the Mn-O bond distance and Mn-O-Mn bond angle, which leads to a stronger interaction and gives a higher Curie temperature<sup>[6,9]</sup>. Based on the thermodynamic theory, the entropy change can be calculated<sup>[9]</sup>. Fig. 1 displays the temperature dependence of the magnetic entropy change ( $\Delta S_M$ ) for

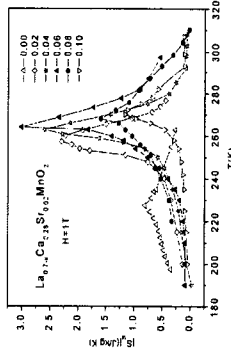


Fig. 1. Temperature dependence of  $\Delta S_M$  for  $\text{La}_{0.7-x}\text{Ca}_{0.28}\text{Sr}_{0.02}\text{MnO}_3$ .

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Recent Development and Current Status of Rare Earth Magnet Research in Japan

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Figure 1 shows the development of (BH)<sub>max</sub> of permanent magnets. After the development of Nd-Fe-B magnets, rare earth magnets are now essential components in many fields of technology. There are two, well-established techniques for the manufacture of rare earth magnets: powder metallurgy is used to obtain high performance, anisotropic, fully dense magnet bodies; and melt-spinning is widely used to produce magnet powders for isotropic bonded magnets. Another technique is the Hydrogenation, Disproportionation, Desorption, and Recombination (HDDR) process, which is effective for the production of high performance, anisotropic bonded magnet powders.

In the industry of sintered Nd-Fe-B magnets in Japan, the total amount of production has increased about 20 % from year to year (Fig. 2). The dominant application has been for voice coil motors (VCM), however, the total amounts has been decreasing because of down sizing of HDD. On the other hand, the applications for motors are now increasing. Especially, the use for the motors in hybrid cars is considered as one of the most attractive applications in Japan. However, Dy addition is needed for the increase of coercivity for the high temperature use in hybrid cars. As the Dy resources are limited, the decrease of Dy content in Nd-Fe-B magnets is strongly demanded.

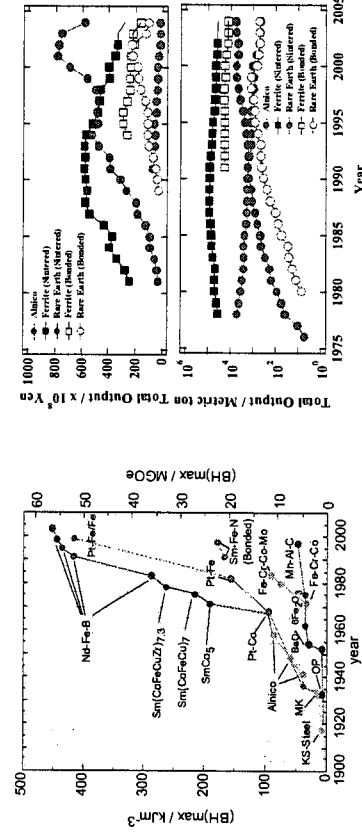


Fig. 1. History of Permanent Magnet.

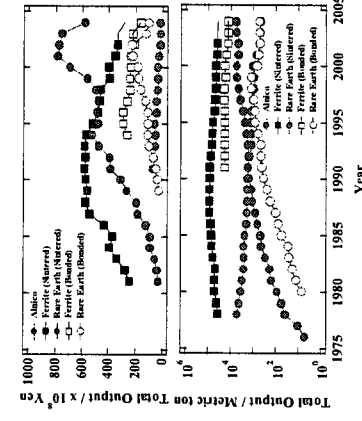


Fig. 2. Trend of sales amount of typical permanent magnet materials in Japan. ( )

In the research of bonded magnets, Sm-Fe-N and anisotropic Nd-Fe-B HDDR magnet powders are now in commercial. The application of the MQ-3 type magnets has also spread. This article reviews the current status and trend in the rare-earth magnet research in Japan.

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[1] Data from the Electronics Materials Manufacturers Association of Japan (EMAJ) and Japan Association of Bonded Magnet Industries.