Magnetocaloric Properties of La0.67Ca0.33-xSrxMnO3± (x [0;0.33])

Dinesen, Anders Reves; Mørup, Steen; Pryds, Nini

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The magnetocaloric properties of a series of Ca- and Sr-doped lanthanum manganites, La$_{0.67}$Ca$_{0.33-x}$Sr$_x$MnO$_3$ ($0 \leq x \leq 0.33$), have been investigated and selected results will be presented. The samples showed a substantial magnetocaloric effect in a temperature range around their respective Curie temperature. By varying the composition parameter $x$ the Curie temperature could be adjusted between 267 K ($x = 0$) and 369 K ($x = 0.33$). The possibility of tailoring a working substance for magnetic refrigeration near room temperature was thereby demonstrated.

Seven La$_{0.67}$Ca$_{0.33-x}$Sr$_x$MnO$_3$ samples (with a variation of $x$ corresponding to an equidistant exchange of Ca with Sr) were synthesized using the glycine-nitrate combustion technique. By x-ray diffraction the samples were found to be single-phase perovskites. The magnetocaloric effect was measured both directly, providing the adiabatic temperature change $\Delta T_{ad}$, and indirectly, providing the isothermal magnetic entropy change $\Delta S_M$ (the entropy change was derived from magnetization measurements).

Figure 1 shows an example of raw data obtained from a direct measurement of the adiabatic temperature change in La$_{0.67}$Ca$_{0.33}$MnO$_3$ (i.e. the sample with $x = 0$). Each step on the temperature curve in Fig. 1a is associated with magnetization and subsequent demagnetization of the sample. Fig. 1b shows an enlarged view of a single magnetization cycle, where the applied field (0.7 T) gives rise to an adiabatic temperature change of about 1.5 K.

**Fig. 1.** (a) Temperature profile for the La$_{0.67}$Ca$_{0.33}$MnO$_3$ sample obtained during a direct measurement of the adiabatic temperature change. (b) Enlarged view of the magnetization cycle outlined in panel (a).
Figure 2 shows the temperature dependence of the magnetic entropy change of the manganite samples due to a field change of 1.2 T. The samples show caret-shaped magnetocaloric peaks with a maximum $|\Delta S_M|$ value at the Curie temperature. The figure thus illustrates the close relationship between the substitution parameter $x$ and the Curie temperature (and thereby the magnetocaloric temperature working range of the compounds). For comparison the entropy change of Gd (the prototypical working substance for magnetic refrigeration at room temperature\(^1\)) is shown in the same figure. Considering the maximum magnetic entropy changes, the values obtained for the $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}_3$ samples with low Ca content are comparable to that of Gd. For the $x = 0$ sample the maximum $|\Delta S_M|$ value exceeds the maximum $|\Delta S_M|$ value of Gd by a factor of 1.7.

![Figure 2](image)

**Fig. 2.** Temperature dependence of the magnetic entropy changes in the $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}_3$ samples due to a field change of 1.2 T. Magnetic entropy change of Gd is shown for comparison (data obtained from reference 2).

The combination of a quite large magnetocaloric effect, excellent chemical stability, and adjustable temperature working range makes $\text{La}_{0.67}\text{Ca}_{0.33-x}\text{Sr}_x\text{MnO}_3$ an interesting candidate as refrigerant in future cooling technology based on the magnetocaloric effect.

REFERENCES