Magnetocaloric effect in nanoparticles of non-stoichiometric manganite

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Obtaining single-phase self-doped non-stoichiometric nanopowder manganites is of a particular interest because of their diverse magnetic state transitions and potential practical applications as magnetic refrigerants and in medicine for treating cancer [1-4]. The determination of the crystal structure, morphology and magnetic properties of different stoichiometric samples is very important for the analysis of the functional properties of manganites.

Methods of Investigation

- X-ray diffraction (XRD) method using Shimadzu LabX XRD-6000 diffractometer in $Cu_{K\alpha 1}$-radiation at room temperature
- Transition electron microscopy (TEM) method using JEM-2200FS Transmission Electron Microscope
- Magnetic method using a Quantum Design SQUID MPMS 3 magnetometer

Results and Discussion

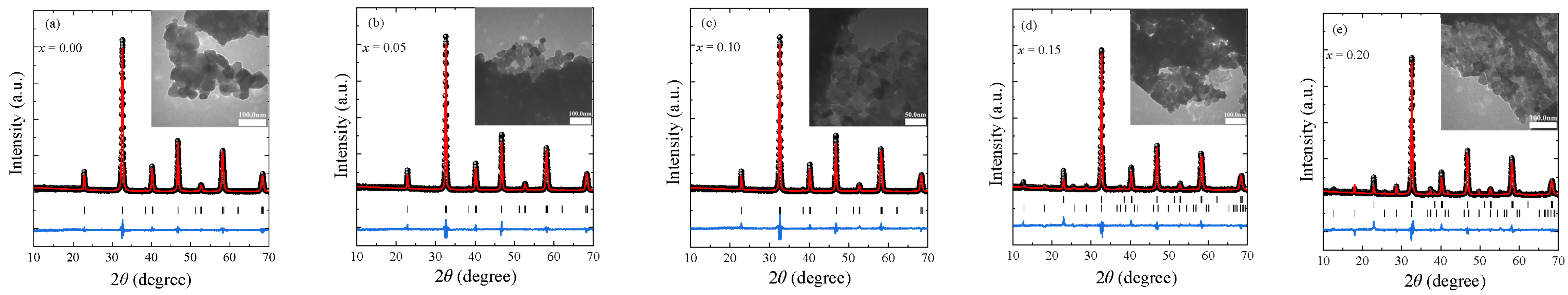

Fig. 1. X-ray patterns and morphology for the $La_{0.8-x}K_{0.2}Mn_{1+x}O_3$ nanopowders.

According to XRD and TEM data, it has been found that the synthesized non-stoichiometric manganites consist of quasi-spherical nanoparticles around 40 nm. The main crystalline phase of all samples is rhombohedral $R\bar{3}c$ perovskite structure. With further increase in concentration at $x > 0.10$, the compositions become non-single phase with negligible amount of Mn_3O_4 impurity.

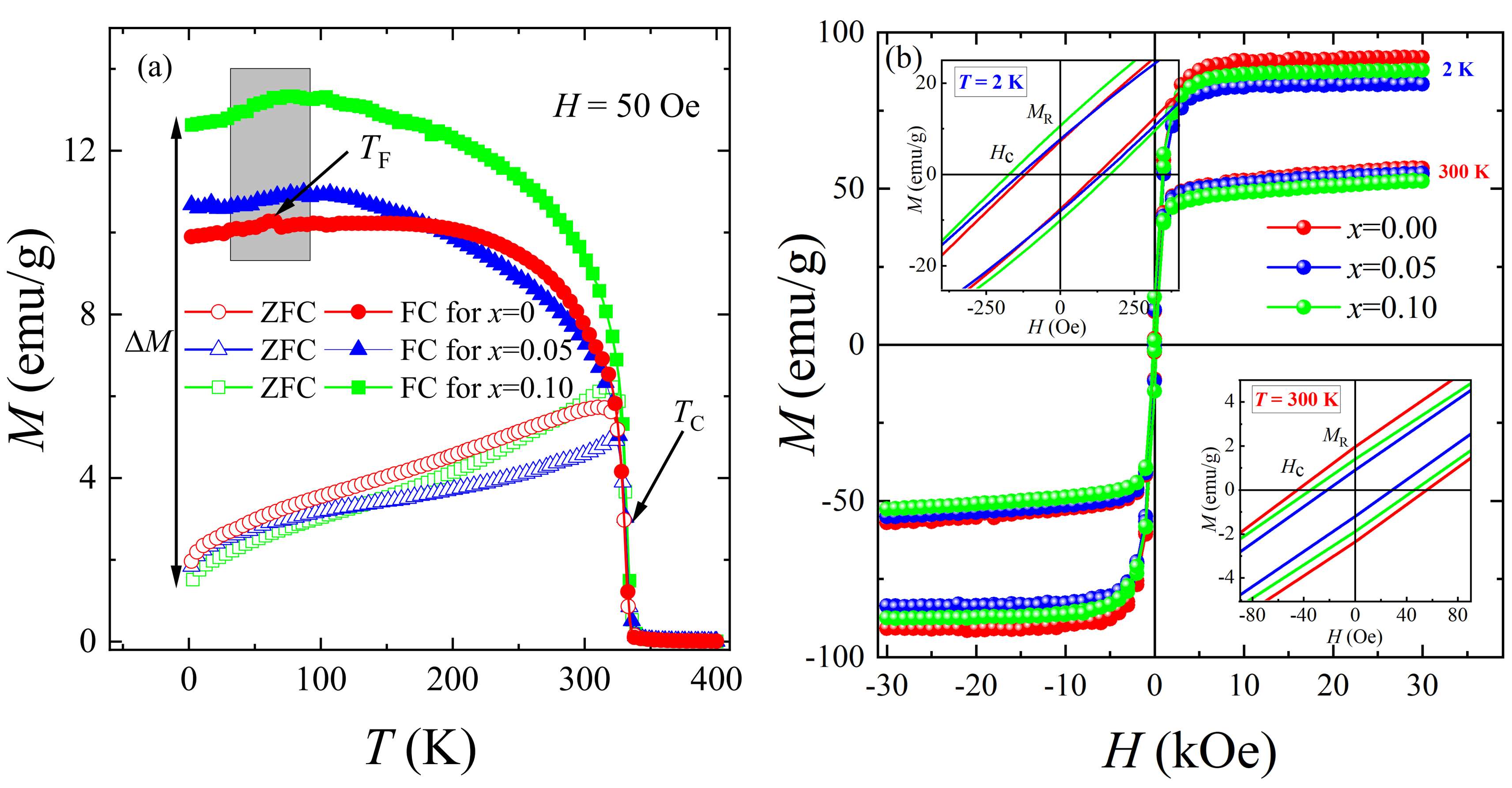

Fig. 2. Temperature (a) and magnetic field (b) dependences of magnetization for the $La_{0.8-x}K_{0.2}Mn_{1+x}O_3$ nanopowders. The inserts of (b) show an enlarged area of hysteresis loops at T = 2 and 300 K to determine coercivity H_C and residual magnetization M_R.

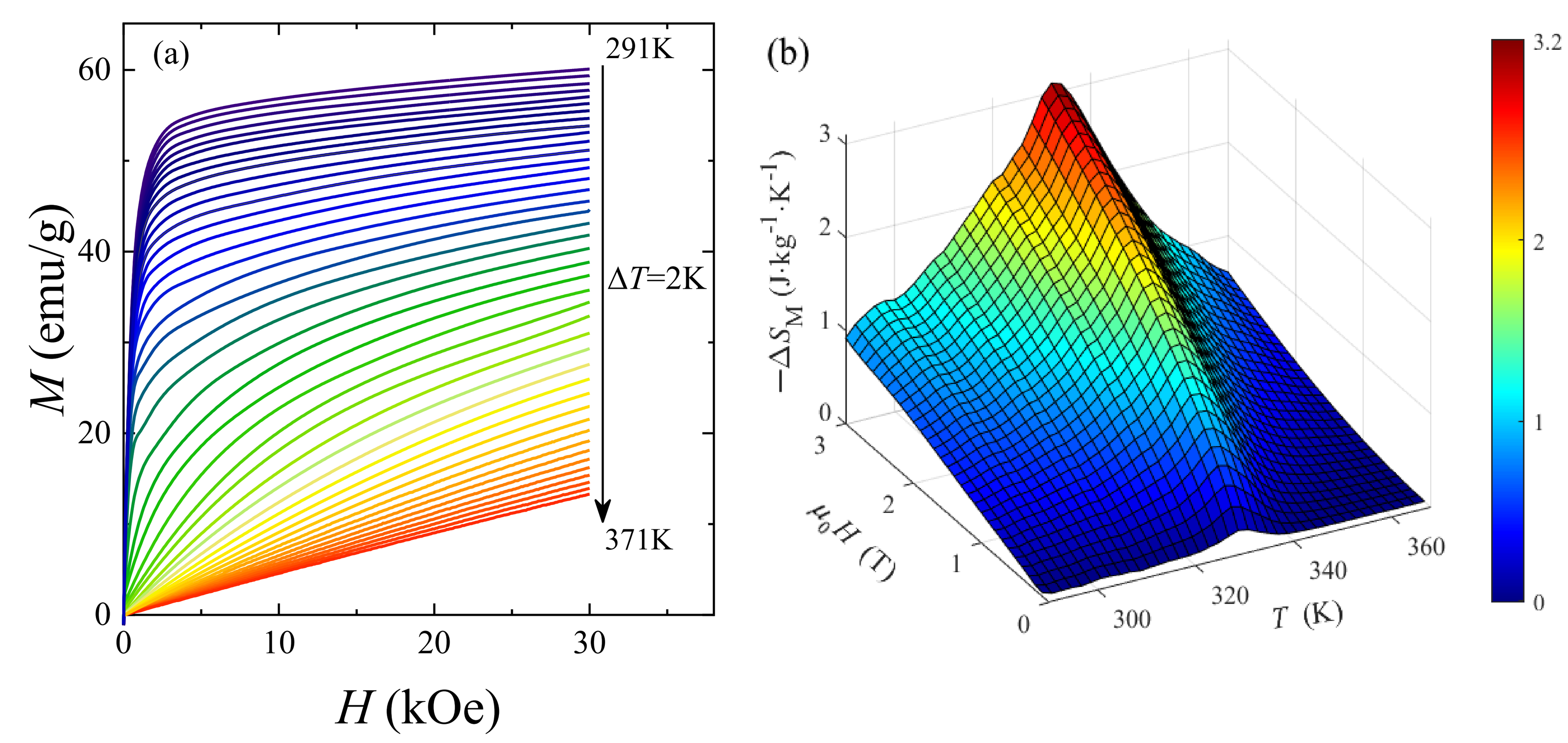

Fig. 3. Isotherms of magnetization within T = 291–371 K (a), as well as temperature and field 3D-dependence of the magnetic entropy change up to $\mu_0 H$ = 3 T (b) for the selected $La_{0.75}K_{0.2}Mn_{1.05}O_3$ nanocrystalline sample.

The magnetic properties and magnetocaloric effect of these compounds were studied as a function of manganese doping level. Magnetic measurements show that the synthesized manganites change from ferromagnetic state to paramagnetic state with the increase of temperature around T_C = 330 K and exhibit the characteristics of typical magnetic nanopowder. The composition with the highest entropy change ΔS_M^{max} = –3.629 J / (kg·K) under 3 T at T_C = 332 K is the $La_{0.8-x}K_{0.2}Mn_{1+x}O_3$ with x = 0.05.

Conclusions

- All samples are crystalized in a rhombohedral $R\bar{3}c$ type of symmetry, the single-phase perovskite structure of which are preserved up to concentration x = 0.10.
- An average size of spherical-like particles changes slightly depending on x and is around 40 nm based on the XRD and TEM data.
- It has been established that excess manganese doping and appearance of cation vacancies in A-positions can significantly improve the ferromagnetic nature and magnetocaloric effect, whereas the magnetic phase transition temperature changes slightly depending on the concentration x.
- The non-stoichiometric $La_{0.75}K_{0.2}Mn_{1.05}$ nanocrystalline sample shows the highest magnetic entropy change ΔS_M^{max} = –3.629 J / (kg·K) under magnetic field 3 T at T_C = 332 K.

References

1. *Arun B., Akshay V. R., Vasundhara M.* Observation of enhanced magnetocaloric properties with A-site deficiency in $La_{0.67}Sr_{0.33}MnO_3$// Dalton Trans.-2018.-**47.**-P.15512.
2. *Phan M. -H., Yu S. -C.* Review of the magnetocaloric effect in manganite materials // J Magn Magn Mater.-2007.-**308.**-P. 325-340.
3. *Wei Ziyu, Pashchenko A.V., Liedienov, N.A. et al.* Multifunctionality of lanthanum–strontium manganite nanopowder// Phys. Chem. Chem. Phys.-2022.-**22**.-P.11817-11828.
4. *Andrade V.M., Vivas R.J.C., et al.* Magnetic and magnetocaloric properties of $La_{0.6}Ca_{0.4}MnO_3$ tunable by particle size and dimensionality // Acta Mater. -2016.-**102**-P.49-55.