Stability of $Ln_3Ba_2Mn_2Cu_2O_{12}$ (Ln = lanthanide) Compounds and Their Magnetic Properties

Ichiro Matsubara,* Ryoji Funahashi, Noriaki Kida,[†] and Kazuo Ueno
Osaka National Research Institute, AIST, Midorigaoka 1, Ikeda, Osaka 563
[†]*Osaka Electro-Communication University, Hatcho, Neyagawa, Osaka 572*

(Received July 31, 1996)

The layered manganocuprate $Ln_3Ba_2Mn_2Cu_2O_{12}$ (Ln = lanthanide) consists of an intergrowth of single rock-salt layers with quadruple oxygen-deficient perovskite layers. This structure is stabilized by a particular ionic size at the Ln site (Ln = Sm, Eu, Gd). The ground state changes from a spin glass to a ferromagnetic phase with decreasing size of the Ln ion (Sm → Gd).

Mixed perovskites with layered ordering arrangement including the cuprates $A'A''CuB'O_{6-\delta}$ are currently of considerable interest as the structure of the high-T_c superconductors. The epoch-making compound $La_2Ba_2Sn_2Cu_2O_{11}$ has been reported by Anderson *et al.* as the first example in which the double layers of square-pyramidal CuO_5 are interleaved with double layers of octahedrally coordinated tin cations, and represents a new family of potential superconductors.[1] The isostructural $Gd_2Ba_2Ti_2Cu_2O_{11}$ (Figure 1, (a)) has been discovered in the course of systematic substitutional study of $La_2Ba_2Sn_2Cu_2O_{11}$.[2] In these layered cuprates, stability depends much on the cation radius of lanthanide ions.[3]

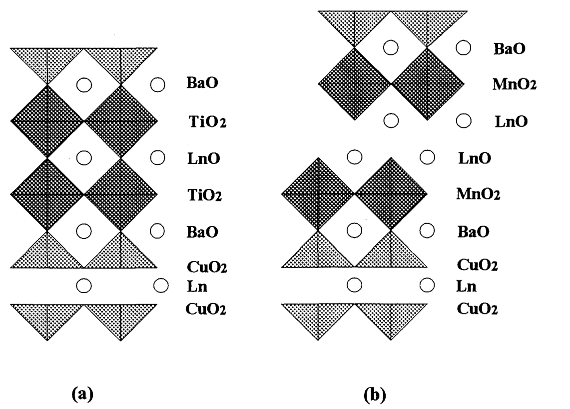

Figure 1. Schematic diagram of (a) $Ln_2Ba_2Ti_2Cu_2O_{11}$ structure and (b) $Ln_3Ba_2Mn_2Cu_2O_{12}$ structure.

More recently, Hervieu *et al.* have reported layered manganocuprate $Eu_3Ba_2Mn_2Cu_2O_{11}$ which consists of an intergrowth of single rock-salt layers with quadruple oxygen-deficient perovskite layers (Figure 1, (b)).[4] The double layers of square-pyramidal CuO_2 are, therefore, separated by K_2NiF_4-type layers, instead of double layers of perovskite units. This structure has been first reported by Fukuoka *et al.* for $Gd_2CaBa_2Ti_2Cu_2O_{12}$,[5] and is thought to signal another new family of potential superconductors. This letter presents the stability of the $Ln_3Ba_2Mn_2Cu_2O_{12}$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Er, Yb) structure as a function of the constituent lanthanides.

Samples of composition $Ln_3Ba_2Mn_2Cu_2O_{12}$ (Ln = lanthanide)

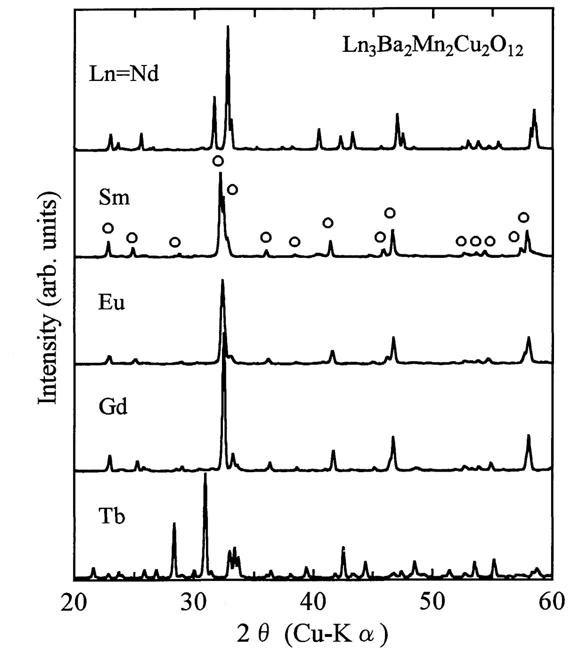

Figure 2. Powder X-ray diffraction patterns of $Ln_3Ba_2Mn_2Cu_2O_{12}$ (Ln = Nd, Sm, Eu, Gd, Tb). Diffraction peaks due to the $Ln_3Ba_2Mn_2Cu_2O_{12}$ structure are marked with an open circle.

were prepared by solid-state reaction using oxides and carbonates as source material, all of purity 99.9% or greater. A well-ground mixture (2 g) of the starting materials was pressed into pellet form and heated in air at 1273 K for 4 h at a heating rate of 2 K/min. After cooling to room temperature, the samples were reground, pelletized, and heated at 1348 K for another 4 h. X-ray powder diffraction data were collected with a Rigaku diffractometer with Cu-Kα radiation. Silicon was employed as an internal standard.

X-ray diffraction patterns for Ln = Nd, Sm, Eu, Gd, and Tb are shown in Figure 2. For Ln = Sm, Eu, and Gd, all the diffraction peaks can be indexed on the basis of a tetragonal $Ln_3Ba_2Mn_2Cu_2O_{12}$ structure (marked with an open circle in the pattern). On the other hand, the stoichiometric reaction of $Nd_3Ba_2Mn_2Cu_2O_{12}$ produced a mixture of $NdMnO_3$, $BaMnO_3$, Nd_2CuO_4, and other impurities. The reactions involving Ln = Tb, Dy, Er, and Yb produced a mixture of $Ln_2Cu_2O_5$, $LnMnO_3$, and $BaMnO_3$. The $Ln_3Ba_2Mn_2Cu_2O_{12}$ structure, even in various conditions of heating temperature (1273 - 1473 K) and heating time (8 - 80 h), was not obtained for these samples.

The phase stability of layered mixed-cation perovskites can be expressed using tolerance factors, $t = (r_A+r_o)/\sqrt{2}(r_B+r_o)$, where r_A and r_B are average ionic radii of the A-site and B-site ions respectively, and r_o is ionic radius of the oxygen ion. For the

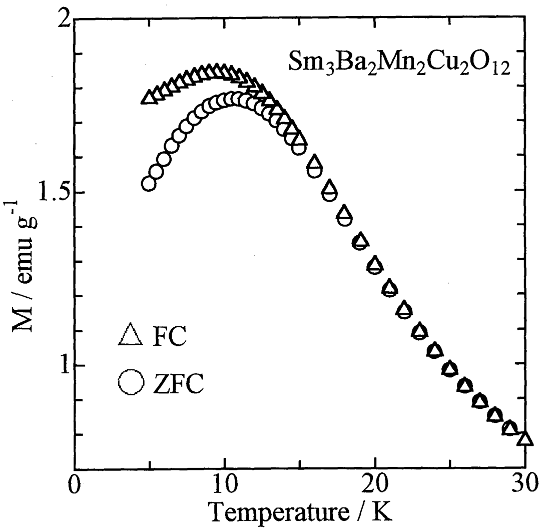

Figure 3. Zero-field-cooled (ZFC: open circle) and field-cooled (FC: open triangle) magnetization curves for $Sm_3Ba_2Mn_2Cu_2O_{12}$.

$Ln_2Ba_2Ti_2Cu_2O_{11}$ phase, it has been reported that the structure is obtained in the range $0.976 \geq t \geq 0.963$.[3] On the other hand, the $Ln_3Ba_2Mn_2Cu_2O_{12}$ structure is stabilized in a narrow range $0.954 \geq t \geq 0.950$. The ionic radii reported by Shannon were used for this calculation.[6] The $Ln_3Ba_2Mn_2Cu_2O_{12}$ is stabilized only in a particular ionic size at the Ln site. Simple perovskite ABO_3 structure allows a wide range of t, usually $0.75 \leq t \leq 1$, because a rotation of BO_6 octahedral and a small displacement of ions cancel the mismatching of cation radii. Such structural flexibility is restricted in the K_2NiF_4 structure due to rigid rock-salt layers. It is well known that difference in Ln ionic radii results in structural difference in the Ln_2CuO_4 compounds, *e. g.*, Nd_2CuO_4 has the T^* structure in contrast to the K_2NiF_4-type of La_2CuO_4. The narrower range of t for the $Ln_3Ba_2Mn_2Cu_2O_{12}$ phase than the $Ln_2Ba_2Ti_2Cu_2O_{11}$ phase is attributed to the presence of rock-salt layers. The c-axis significantly increases with Ln from 3.5140(3) nm (Ln = Gd) to 3.5454(8) nm (Ln = Sm), while the a-axis is nearly independent of Ln. The elongation of the c-axis can be explained quantitatively by the Ln ionic radii.

The temperature dependence of magnetization was measured using a superconducting quantum interference device magnetometer. Figure 3 shows the temperature dependence of magnetization for $Sm_3Ba_2Mn_2Cu_2O_{12}$ measured with a field of 0.3 T after cooling down to 5 K in the magnetic field (FC) and in the zero field (ZFC). Below 15 K, the FC curve starts to deviate from the ZFC curve, which is characteristic of a spin glass transition.[7] Such hysteresis behavior was not observed for Ln = Eu and Gd samples, which show a ferromagnetic transition at T < 25 K evident from hysteresis behavior in the M-H curve. The ground state changes from a ferromagnetic (Ln = Gd, Eu) to a spin glass (Ln = Sm) phase.

In our preliminary experiments, the substitution of Zn for Cu in $Eu_3Ba_2Mn_2Cu_2O_{12}$ did not affect the magnetization, whereas the substitution of Sc for Mn changed the ferromagnetic magnetization to a paramagnetic one. Therefore, the observed magnetic behavior derives chiefly from manganese which is in a mixed valence state according to the formula $Ln_3Ba_2Mn^{3+}Mn^{4+}Cu_2O_{12}$.[4] In the systematic study of K_2NiF_4-type $La_{1-x}Sr_{1+x}MnO_4$, a spin glass phase due to the competition between the antiferromagnetic superexchange interaction and the ferromagnetic double-exchange interaction has been observed for $x \geq 0.2$.[8] These competitive interactions are thought to exist in the $Ln_3Ba_2Mn_2Cu_2O_{12}$ compounds. It has been reported that magnetic correlation between the B-site cations is affected by the size of the A-site cation in the K_2NiF_4-type oxides.[9] A small Ln ion reduces the c-axis lattice parameter of the $Ln_3Ba_2Mn_2Cu_2O_{12}$ structure, resulting in an increase of MnO_2 interlayer coupling. The improved three-dimensional character strengthens the ferromagnetic interaction due to an increased itinerary of the carrier in the c-axis direction. This effect results in the change of ground state from a spin glass to a ferromagnetic phase with decreasing size of the Ln ion (Sm → Gd). The Ln ionic size is an important factor for the stability and the magnetic properties of mixed perovskites with layered ordering arrangement.

References and Notes

1 D. T. Anderson, K. R. Poeppelmeier, J.-P. Zhang, H.-J. Fan, and L. D. Marks, *Chem. Mater.*, **4**, 1305 (1992).
2 A. Gormezano and M. T. Weller, *J. Mater. Chem.*, **3**, 771 (1993).
3 K. B. Greenwood, G. M. Sarjeant, K. R. Poeppelmeier, P. A. Salvador, T. O. Mason, B. Dabrowski, K. Rogacki, and Z. Chen, *Chem. Mater.*, **7**, 1355 (1995).
4 M. Hervieu, C. Michel, R. Genouel, A. Maignan, and B. Raveau, *J. Solid State Chem.*, **115**, 1 (1995).
5 A. Fukuoka, S. Adachi, T. Sugano, X. -J. Wu, and H. Yamauchi, *Physica C*, **231**, 372 (1994).
6 R. D. Shannon, *Acta Crystallogr.*, **Sect. A 32**, 751 (1976).
7 K. Binder and A. P. Young, *Rev. Mod. Phys.*, **58**, 801 (1986).
8 Y. Moritomo, Y. Tomioka, A. Asamitsu, Y. Tokura, and Y. Matsui, *Phys. Rev. B*, **51**, 3297 (1995).
9 P. Ganguly and C. N. R. Rao, *J. Solid State Chem.*, **53**, 193 (1984).