Synthesis and Application of $[Mo_8O_{16}Cl_2(OCH_3)_6(HOCH_3)_4]$ to Magnetoresistant Oxides

Hee K. Chae,* Jung Young Kim, Chulsoon Hwang, and Bo Wha Lee†
Department of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Korea
†*Department of Electronic Physics, Hankuk University of Foreign Studies, Yongin 449-791, Korea*

(Received March 12, 2002; CL-020239)

An octanuclear oxomolybdenum(V) cluster compound $[Mo_8O_{16}Cl_2(OCH_3)_6(HOCH_3)_4]$ was prepared from the reaction of oxomolybdenum(V) chloride and the potassium salt of triethanolamine in methanol. The complex was used to prepare Sr_2FeMoO_6, which shows a very high negative magnetoresistance of 33% with a magnetic field of 0.8 T at 12 K.

The colossal magnetoresistance (CMR) in perovskite oxides including doped manganates[1] has attracted great attention. But it is questionable whether these compounds would be useful for most applications, because the high values of magnetoresistance (MR) only occur with magnetic fields as high as 7 T and/or temperatures as low as 5 K. Recently, the ordered double perovskite Sr_2FeMoO_6 has been reported to have a low-field MR at room temperature (RT) and a high Curie temperature over 400 K.[2] The large MR, however, can be obtained only in high magnetic fields of several tesla at RT. For magnetic recording devices, magnetic materials should have a large MR at low fields and ambient temperatures. The sol-gel process is one of the candidate methods used to enhance the low field MR of Sr_2FeMoO_6 because of relatively easy control of particle size with high purity and homogeneous stoichiometry.[3] Even though a limited number of the sol-gel methods are reported for the preparation of mixed-metal perovskite magnetic oxides, the study of the molybdenum alkoxide or oxoalkoxide precursors to molybdenum oxides remains relatively unexplored.[4] A few attempts have been made to prepare $A_2Fe^{III}Mo^{V}O_6$ (A = alkaline earth ions) from Mo(VI) ionic complexes including $(NH_4)_6Mo_7O_{24}$ rather than well-characterized Mo(V) alkoxide precursors.[3b] When water-soluble nitrate or ammonium salts are used as starting materials, some additives should be included as gelificant agents.[3] In the case of well-characterized alkoxide starting materials, however, it is not necessary to add the additive that may cause unexpected stoichiometric unbalance in the final product. Here, we demonstrate the preparation and structural characterization of an octamolybdenum(V) oxoalkoxide precursor, and its application to low-field, high MR and polycrystalline Sr_2FeMoO_6 by sol-gel process.

The molybdenum precursor complex $[Mo_8(O)_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_4(\mu_3\text{-}OCH_3)_2(\mu_2\text{-}OCH_3)_4Cl_2(HOCH_3)_4 \cdot 6(CH_3OH)]$ (**1**) was prepared the addition of brown $Mo(O)Cl_3$ (1.00 g, 4.58 mmol) in 100 mL of methanol to the colorless solution of $K_3[(OCH_2CH_2)_3N]$ (1.20 g, 4.77 mmol) in 50 mL of methanol at room temperature. The resulting orange solution was decanted and set aside at 4 °C for 7 d to give pink crystals of complex **1** (2.02 g, 1.26 mmol) with 27.5% yield based on molybdenum.[5] The crystallographic analysis of **1** shows the presence of a neutral Mo(V) complex in which four $Mo^{V}(O)(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}OCH_3)$-$Mo^{V}(O)(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}OCH_3)$ dimers are bound to share edges each other as depicted in Figure 1.[6] Each molybdenum atom has one solvated methanol and/or one chloride. Two chains of four octahedra Mo are fused to form a chain structure, which is similar to chains of $MoO_5(OH_2)$ octahedra in the structure of α-$MoO_3 \cdot H_2O$. Addition of base to $[MoOCl_5]^{2-}$ yields a brown precipitate that is often formulated as $[MoO(OH)_3]$ but no structural information is available for this substance or any $[Mo_2O_5]$ species, even though mixed-valence oxides are well-characterized crystallographically including rhombohedral and monoclinic phases of Mo_8O_{23} ($7MoO_3 \cdot MoO_2$).[7a] Thus, **1** may provide useful information about pure ''Mo(V) oxide'' phases.

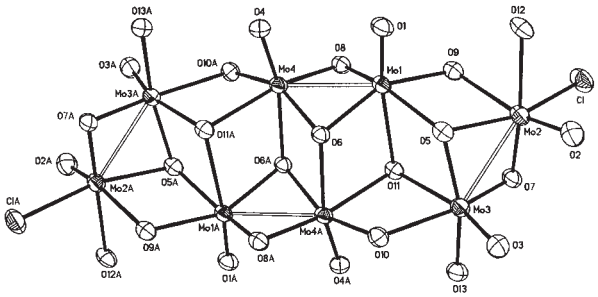

Figure 1. ORTEP drawing of $[Mo_8(O)_{12}(\mu_3\text{-}O)_6(\mu_2\text{-}O)_8Cl_2]$ core of **1**. Selected bond lengths (Å) and angles (°): Mo(1)–O(1), 1.680(3); Mo(1)–O(5), 2.106(3); Mo(1)–O(6), 1.977(3); Mo(1)–O(11), 2.416(3); Mo(1)–Mo(4), 2.5678(6); O(1)–Mo(1)–O(6), 105.87(14); O(1)–Mo(1)–O(11), 167.00(14), O(1)–Mo(1)–Mo(4), 96.67(12).

As far as we know, the structure of **1** is unique, even though the tetranuclear core cluster moiety of **1** is a well-known structural motif in polyoxomolybdates, especially Mo(VI) complexes. There are a number of octanuclear molybdate species in polyoxomolybdates,[7] based on the β-molybdate(VI), $[Mo_8O_{28}]^{8-}$ structure including $[Mo_8O_{24}(OMe)_4]^{4-}$, $[Mo_8O_{26}(HCO_2)_2]^{6-}$ and $[Mo_8O_{24}(sal)_2]^{2-}$ (sal = salicylidenepropyliminato). Relatively few examples of Mo(V) clusters are known; $[Mo_8O_{16}(OMe)_8(C_2O_4)]^{4-}$, $[Mo_8O_{16}(OMe)_8(PR_3)]$ and $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu_2\text{-}OH)_4(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_4]$-$(HOEt)_4]$.[8] The first two clusters exhibit a cyclic framework, while the last one shows the cubane-like distorted rutile structure. However, the structure of **1** shows a two-dimensional extended framework with six μ_3-O coordinations, which is quite different from those of three above complexes.

Polycrystalline samples of Sr_2FeMoO_6 were prepared by sol-gel process using strontium 2-methoxyethoxide, iron 2-methoxyethoxide and **1** in a metal-based ratio of 2 : 1 : 1 in 2-methoxyethanol.[9] The hydrolyzed precipitate was calcined at 850 °C in air before the powder was pressed into pellets. Samples A, B, and C were sintered at temperatures of 875, 900 and 1100 °C in a stream of 5% H_2/Ar for two h, respectively. Each

polycrystalline phase was confirmed by X-ray powder diffraction pattern. The diffraction peaks are indexed with respect to the cubic symmetry (*Fm3m*) with a slight tetragonal distortion.

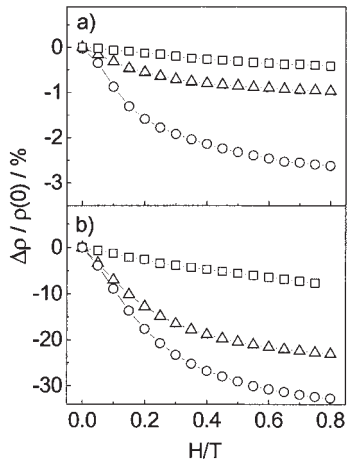

Figure 2. Magnetoresistance of polycrystalline Sr_2FeMoO_6 samples A(◯), B(△), and C(□) for different sintering temperatures measured at (a) 300 K and (b) 12 K.

Preliminary MR investigations of the sample are shown in Figure 2. The magnitude of negative MR for sample A with the magnetic field of 0.8 T at 12 and 300 K is as large as 33 and 2.5%, respectively. In the case of metallic sample C, the magnitude of MR is smaller than those of semiconducting samples A and B. Since the field dependent magnetization is almost the same for both metallic and semiconducting samples, the discrepancy in MR is not due to a bulk phenomenon. It is a consequence of grain boundary scattering due to different grain size formed at different sintering temperature. The resulting grain size increases from 0.5 μm for sample A to 2 μm for sample C, which was estimated from scanning electron micrographs. Individual moments are aligned by the external magnetic field and the hopping of the spin-polarized electron between grains is controlled by the external field. Therefore the large MR observed in the semiconducting sample is due to the enhanced intergrain tunneling by reducing the relative angle of magnetization directions at the grain boundaries.

The work was supported by Hankuk University of Foreign Studies Research Fund of 2002. We are also grateful to Prof. O. M. Yaghi and Dr. Jaheon Kim at University of Michigan for X-ray facilities.

References and Notes

1 a) S, Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, *Science*, **264**, 413 (1994). b) "Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides," ed. by C. N. R. Rao and B. Raveau, World Scientific, Singapore (1998), and references therein.

2 K. I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature*, **395**, 667 (1998).

3 a) J. Mahia, C. Vazquez, J. Mira, A. Lopz-Quintela, J. Rivas, T. E. Jones, and S. B. Oseroff, *J. Appl. Phys.*, **75**, 6757 (1994). b) C. L. Yuan, S. G. Wang, W. H. Song, T. Yu, J. M. Dai, S. L. Ye, and Y. P. Sun, *Appl. Phys. Lett.*, **75**, 3853 (1999).

4 a) H. K. Chae, C. Hwang, Y. Dong, H. Yun, and H. G. Jang, *Chem. Lett.*, **2000**, 992. b) H. Han, B. J. Han, J. S. Park, B. W. Lee, and C. S. Kim, *J. Appl. Phys.*, **89**, 7687 (2001). c) J. Attner, and U. Radius, *Chem.—Eur. J.*, **7**, 783 (2001). d) M. Nagano and M. Greenblatt, *J. Non-Cryst. Solids*, **101**, 255 (1988).

5 FT-IR (KBr pellet, cm^{-1}): 3433(br), 2933(w), 1632(br), 1030(w), 970(s), 717(m), 681(m), 550(m), 519(m), 494(m), 464(w). Anal. Calcd. for $C_{16}H_{58}O_{32}Cl_2Mo_8$: C, 12.00; H, 3.66; Cl, 4.43%. Found: C, 11.76; H, 3.49; Cl, 4.61%.

6 Pink rod-shape crystals of **1** were analyzed at 208 ± 1 K: triclinic, space group $P(-1)$ with $a = 7.8373(4)$ Å, $b = 10.1107(5)$ Å, $c = 15.0384(7)$ Å, $\alpha = 92.9500(10)^\circ$, $\beta = 98.4170(10)^\circ$, $\gamma = 92.2460(10)^\circ$, $V = 1175.94(10)$ Å^3, $Z = 1$, $d_{calcd} = 2.261$ g/cm^3, μ_a(Mo Kα) $= 2.263$ mm^{-1}, goodness of fit on $F^2 = 1.000$, $R = 0.0351$ and $R_w = 0.0884$. Crystallographic details and complete listings have been deposited at the Cambridge Crystallographic Data Center (Deposition No. CCDC-183930).

7 a) M. T. Pope, in "Progress in Inorganic Chemistry," ed. by S. J. Lippard, Wiley & Sons, New York (1991), Vol. 39, p 181 and references therein. b) M. I. Khan and J. Zubieta, in "Progress in Inorganic Chemistry," ed. by K. D. Karlin, Wiley & Sons, New York (1995), Vol. 43, p 1 and references therein.

8 a) A. J. Blake, S. Parsons, C. Limberg, and S. Parsons, *J. Chem. Soc., Dalton Trans.*, **1995**, 3263. b) C, Limberg, A. J. Downs, A. J. Blake, and S. Parsons, *Inorg. Chem.,* **35**, 4439 (1996).

9 Y. Kim, H. K. Chae, K. S. Lee, and W. I. Lee, *J. Mater. Chem.*, **8**, 2317 (1998).