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New ferromagnets of $\text{Sr}_8A\text{Re}_3\text{Cu}_4\text{O}_{24}$ ($A = \text{Sr}, \text{Ca}$) with an ordered perovskite structure

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Abstract

New phases $\text{Sr}_8A\text{Re}_3\text{Cu}_4\text{O}_{24}$ ($A = \text{Sr}, \text{Ca}$) were discovered under high-pressure/high-temperature condition. X-ray powder diffraction and electron diffraction studies for these phases indicated that they have an ordered perovskite-type structure with cubic lattices of $\sim 8 \text{ \AA}$. They showed ferromagnetism at room temperature when they were synthesized under high-oxygen-pressure condition. The Ca-containing phase has a very high T_c of 440 K with a spontaneous magnetization of $\sim 1 \mu_B/\text{f.u.}$

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1. Introduction

Perovskite oxides have a general formula of ABO_3 in which the A -site is occupied by a large-size electro-positive cation while the B -site by a small transition metal ion. The B -sites are not always occupied by one kind of cations but sometimes by two or more kinds of cations in an ordered way. Thus far, a huge number of ordered perovskites have been prepared and reported [1]. Recently, ordered double perovskites, $A_2\text{FeMO}_6$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$; $M = \text{Mo}, \text{Re}$), have attracted many a researcher's attention because of their interesting physical properties. The Ba- and Sr-analogues of this family are ferromagnetic metals, and a polycrystalline ceramic sample of the Sr-analogues show magnetoresistance even at room temperature and under a low magnetic field [2–4]. These interesting properties originate from their half-metallic (single-spin) characters [2–3]. On the other hand, a Ca-analogue of $\text{Ca}_2\text{FeReO}_6$ is known to be an insulating ferromagnet with quite high T_c of 538 K [5]. (See Ref. [6] and references therein for further details of magnetism in the $A_2\text{FeMO}_6$ double perovskites.)

Our original idea of the present study was to prepare an ordered double perovskite, $\text{Sr}_2\text{CuReO}_6$, which has not been reported as far as we know. Generally speaking, high-pressure condition is favorable to stabilize a perovskite-type ABO_3 oxide because it is composed of cubic closest packing of A and O atoms. In the present study, we carried out phase search experiments under a high pressure of 6 GPa for Sr–Re–Cu–O and Sr–Ca–Re–Cu–O systems, expecting a new perovskite material. Indeed, we have discovered new ordered perovskites $\text{Sr}_8A\text{Re}_3\text{Cu}_4\text{O}_{24}$ ($A = \text{Sr}, \text{Ca}$) though they are not double perovskites but their B -site cations are ordered in a different way. Interestingly, these phases show ferromagnetism at room temperature when they are prepared under high-oxygen-pressure condition. Their structural and magnetic properties are presented.

2. Experimental

SrO_2 , ReO_3 (99.9%), CuO (99.9%), Sr_2CuO_3 and SrCuO_2 were used as starting materials for the Sr–Re–Cu–O samples, while SrO_2 , ReO_3 , CaO , CuO , Sr_2CuO_3 and SrCuO_2 for the Sr–Ca–Re–Cu–O samples. SrO_2 was prepared through a wet process [7] and CaO by a

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decomposition of CaCO_3 (99.9%) at 1000°C . SrCuO_2 and Sr_2CuO_3 were prepared in advance by solid-state reactions in air between SrCO_3 (99.9%) and CuO . Appropriate amounts of the starting materials were mixed in an agate mortar and sealed into a gold capsule. By adjusting the mixing ratios of the starting materials, we could change not only the metal contents but also the oxygen content independently. All procedures were performed in a glove box to avoid contamination of carbon dioxide and water in air. The mixtures were allowed to react in a belt-type high-pressure apparatus for 1–3 h at 6 GPa and 1300 – 1350°C , followed by quenching to room temperature before releasing pressure. The weight of the gold capsule was checked before and after the high-pressure run. The weight change was always less than 0.2 mg against the sample weight of ~ 300 mg. Therefore, the oxygen release did not occur during the high-pressure treatment and the net oxygen content in the starting mixture was kept unchanged.

X-ray powder diffraction (XRD) data were collected using a powder diffractometer (Phillips PW 1800) with $\text{CuK}\alpha$ radiation. Lattice constants were determined by the least-squares method. XRD Rietveld analysis was performed using a program RIETAN-2000 [8]. Transmission electron microscopy observations were carried out for a selected sample by a microscope (Hitachi H-1500) operating at 800 kV. Electron probe microanalysis (EPMA) was done using an angular-dispersion analyzer (JEOL JXA-8600 MX) for a selected sample to know cation ratios of a high-pressure phase. In EPMA, a small ceramic specimen was well polished using diamond paste to obtain a flat surface of $2 \times 2 \text{ mm}^2$ and, several relatively large grains were selected and analyzed. Magnetic measurements were carried out using a SQUID magnetometer (Quantum Design, MPMS) for a lower temperature region and using a vibrating sample magnetometer (VSM, PAR155) for a higher temperature region.

3. Results and discussion

3.1. Synthesis, phase identification and structure analysis

About 50 and 20 starting mixtures were tested for the Sr–Re–Cu–O and Sr–Ca–Re–Cu–O systems, respectively. Some of these high-pressure samples showed ferromagnetism at room temperature. From synthesis experiments of various samples of the Sr–Re–Cu–O system, it was found that the system contains an unknown phase whose XRD pattern is fairly simple. In the lower part of Fig. 1, XRD pattern of a sample with a nominal composition of $\text{Sr}_{1.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_{3.0}$ is shown. The peaks in this pattern could be indexed assuming a simple cubic lattice with $a = 8.07(1) \text{ \AA}$. This sample had the best phase purity on the phase in

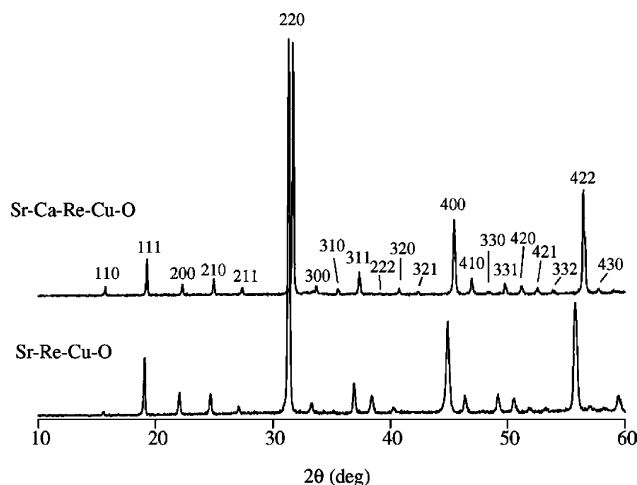


Fig. 1. X-ray powder diffraction patterns of the high-pressure samples with nominal compositions of $\text{Sr}_{1.0}\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5}\text{O}_{3.15}$ (upper part) and $\text{Sr}_{1.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_{3.0}$ (lower part).

question among various starting compositions that we tested. An isostructural phase was found in the Sr–Ca–Re–Cu–O system. The best phase purity was attained in this case for a nominal composition of $\text{Sr}_{1.0}\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5}\text{O}_{3.15}$. The XRD pattern of the Ca-containing sample (the upper part of Fig. 1) could be indexed by a cubic lattice of $7.97(1) \text{ \AA}$ which is slightly smaller than that of the Ca-free phase. The samples shown in Fig. 1 were almost of single phase but trace amount of impurities were included in them though not visible in Fig. 1.

In order to confirm the cubic unit lattice, electron diffraction patterns were observed for the Ca-free phase because it was nonmagnetic (see below) and suitable for the electron microscope observation. Fig. 2 shows electron diffraction patterns projected along the [001] and [111] directions. The pattern projected along [111] has six-fold rotation symmetry (three-fold rotation symmetry in the real structure) confirming the cubic lattice. No systematic extinction is observed in the patterns indicating a space group of $Pm\bar{3}m$ (No. 221) if we select the highest symmetry group.

The nominal compositions of the Ca-free and Ca-containing phases mentioned above may be rewritten as $\text{Sr}(\text{Sr}_{0.15}\text{Re}_{0.35}\text{Cu}_{0.5})\text{O}_{3.0}$ and $\text{Sr}(\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5})\text{O}_{3.15}$, respectively. They suggest the perovskite-type composition of ABO_3 with the *A*-sites occupied by the Sr atoms and the *B*-sites by the three metals of Sr (Ca), Re and Cu. On the other hand, their lattice parameters ($\sim 8 \text{ \AA}$) imply double periodicity along all the three axes of the perovskite lattice, i.e., $a = 2a_p$, $b = 2b_p$, $c = 2c_p$, for the perovskite lattice of a_p , b_p , c_p .

According to the above consideration, Rietveld analysis of the XRD pattern was carried out for the Ca-containing sample of $\text{Sr}(\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5})\text{O}_{3.15}$. Fig. 3 shows our structure model for the Rietveld

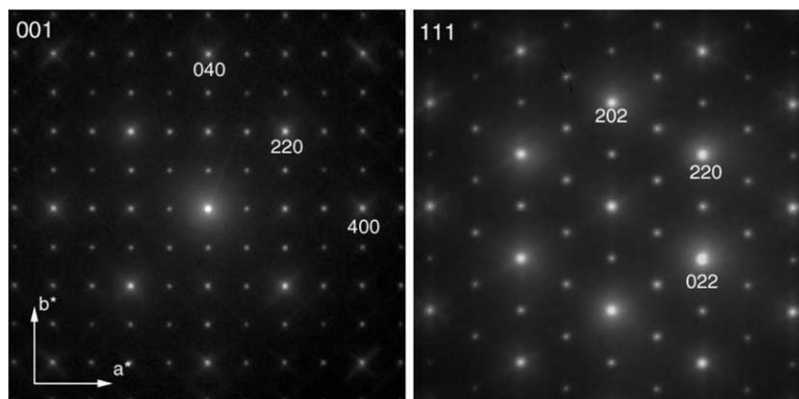


Fig. 2. Electron diffraction patterns of the Ca-free phase projected along the [001] and [111] directions.

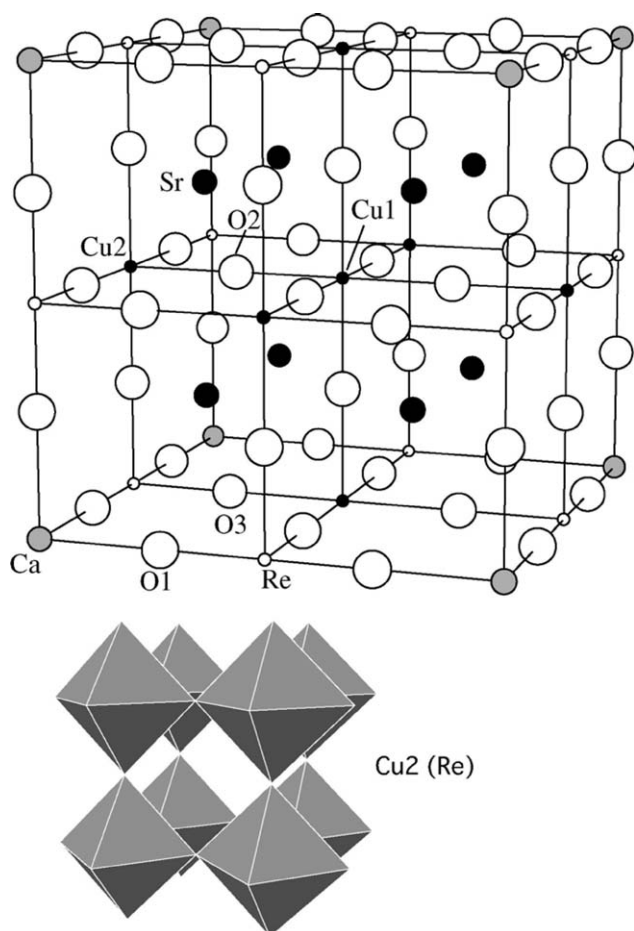


Fig. 3. Crystal structure of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. The lower part indicates a network of the Cu2 (or Re) sites.

analysis which was constructed based on the space group $Pm\bar{3}m$. In this model, the unit cell consists of eight perovskite-like subcells and the A -sites of the subcells are occupied exclusively by Sr. The B -sites are occupied by Ca, Re and Cu in an ordered way, i.e., Ca at the $1a$ sites, Re at the $3d$ sites and Cu at the $1b$ and $3c$ sites. The Rietveld refinement based on this model

was quite successful to result in reliability factors of $R_{\text{wp}}=6.96$ and $R_1=5.64$. Observed and calculated X-ray patterns, final structure parameters and selected bond lengths are shown in Fig. 4 and Tables 1 and 2, respectively.

From the structure model in Fig. 3, a stoichiometric composition of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ is derived for the Ca-containing phase and the unit cell includes one formula unit ($z=1$). This composition is converted to $\text{Sr}(\text{Ca}_{0.125}\text{Re}_{0.375}\text{Cu}_{0.5})\text{O}_3$ and is slightly different from the nominal one of $\text{Sr}(\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5})\text{O}_{3.15}$ from which we obtained the best phase purity. If Ca is simply replaced by Sr in Fig. 3, the stoichiometric composition of the Ca-free phase becomes $\text{Sr}_9\text{Re}_3\text{Cu}_4\text{O}_{24}$ ($\text{Sr}_{1.125}\text{Re}_{0.375}\text{Cu}_{0.5}\text{O}_3$) and this is also slightly different from the “best” nominal composition of $\text{Sr}_{1.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_3$.

In the Rietveld analysis, we refined the occupation factors for the B -site atoms of Ca, Re and Cu. However, they converged to unity within a few percent uncertainties confirming the stoichiometric composition. The EPMA measurement for the Ca-containing phase gave a composition of $\text{Sr}_{1.0}\text{Ca}_{0.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_y$, where the experimental error is the order of ~ 0.01 . This composition is closer to the stoichiometric composition than the nominal one but the Ca/Re ratio is still larger than 1/3 beyond the experimental uncertainty. This may suggest partial substitution of Ca for Re. Magnetic properties of the phases depend drastically on the nominal oxygen content (see below). This fact seems to indicate the possibility of oxygen-vacancy introduction under a low-oxygen-pressure synthesis condition. We did not constrain any temperature factors, and the temperature factors of the oxygen sites, in particular, those of O1 and O3 become noticeably large (Table 1) which may suggest that these sites are partially vacant. In addition, the temperature factor of the Ca site is considerably small. However, by the X-ray powder diffraction pattern alone, it is hard to elucidate more details of the structure. Neutron diffraction study is in progress and

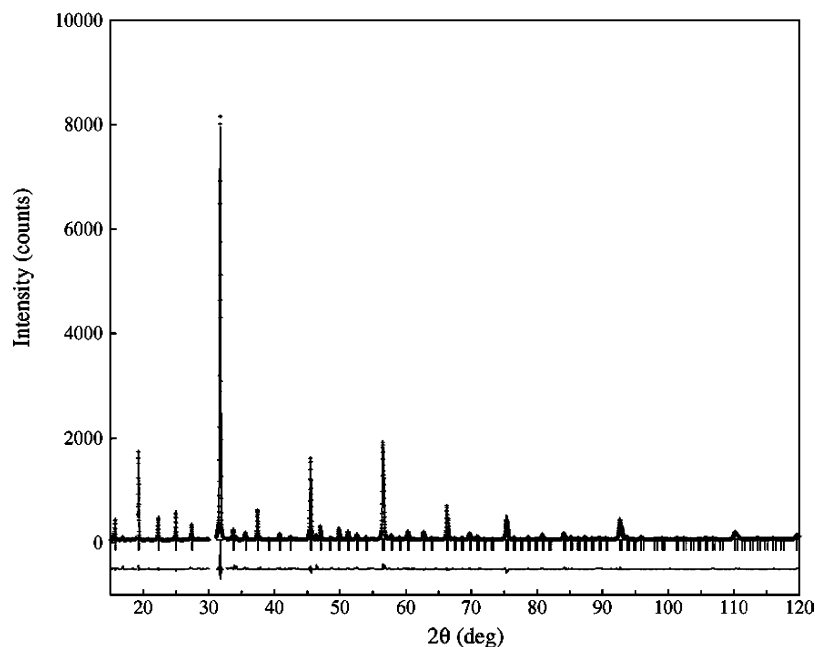


Fig. 4. Observed (cross) and calculated (solid line) X-ray diffraction patterns of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$. Tick marks indicate the positions of allowed Bragg reflections. The difference line, observed minus calculated, is located at the bottom of the figure.

Table 1
Structural parameters of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$

Atom	Site	x	y	z	B (\AA^2)
Ca	1a	0	0	0	0.278(4)
Cu1	1b	1/2	1/2	1/2	0.584(7)
Cu2	3c	0	1/2	1/2	0.85(1)
Re	3d	1/2	0	0	0.656(8)
Sr	8g	0.26994(9)	0.26994	0.26994	1.10(1)
O1	6e	0.271(2)	0	0	9.5(1)
O2	6f	0.252(1)	1/2	1/2	2.91(4)
O3	12h	0.234(1)	1/2	1/2	7.01(9)

$\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ space group: $Pm\bar{3}m$

Lattice parameters: $a = 7.971(8)$ \AA

Reliability factors: $R_{\text{wp}} = 6.96$, $R_1 = 5.64$

Occupation factor is unity for the all atoms.

Table 2
Selected bond lengths (\AA) in $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$

Ca–O1	2.16(2)	Re–O1	1.82(2)
Cu1–O2	1.974(8)	Re–O3	1.86(1)
Cu2–O2	2.012(8)	Sr–O1	3.043(3)
Cu2–O3	2.12(1)	Sr–O2	2.597(3)
		Sr–O3	2.842(3)

it will be helpful for further consideration of the structure.

3.2. Magnetic properties

Magnetic properties were mainly measured for the Ca-containing sample with the nominal composition of

$\text{Sr}(\text{Ca}_{0.175}\text{Re}_{0.325}\text{Cu}_{0.5})\text{O}_{3.15}$ which was ferromagnetic at room temperature. To calculate molar magnetic quantity, we assumed $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$ (stoichiometric composition) as the formula unit. As stated above, there is some uncertainty on the composition of the phase. However, the difference between the molecular weights calculated for the nominal composition and for the stoichiometric one is only ca. $\sim 3\%$ and does not cause serious error. A magnetization curve measured at 5 K is given in Fig. 5 where typical ferromagnetic behavior is seen. Magnetization was saturated above ~ 5000 Oe and a small hysteresis loop was observed. In order to obtain variation of the spontaneous magnetization M_s as a function of temperature, magnetization curves were measured at various temperatures as shown in Fig. 6. From the extrapolation of high-field data to $H=0$, M_s was obtained and is plotted against temperature in Fig. 7. In Fig. 7, a small anomaly is seen near 120 K. However, we did not observe the corresponding anomaly when the magnetization was measured with decreasing temperature. The anomaly is probably due to some experimental problem.

The spontaneous magnetization at $T=0$, M_0 , is estimated to be $\sim 0.95 \mu_B/\text{f.u.}$ from this figure. High-temperature magnetization data measured at 1 kOe by VSM are also shown in Fig. 7 which indicate T_c as high as 440 K. So far, a very limited number of cuprate ferromagnets have been known; rare examples are $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ ($T_c = 5$ K) [9], K_2CuF_4 ($T_c = 6.5$ K) [10] and SeCuO_3 ($T_c = 26$ K) [11], etc. in which Cu–O–Cu (or Cu–F–Cu) bond angles are far less than 180° with a ferromagnetic interaction between the Cu moments. The

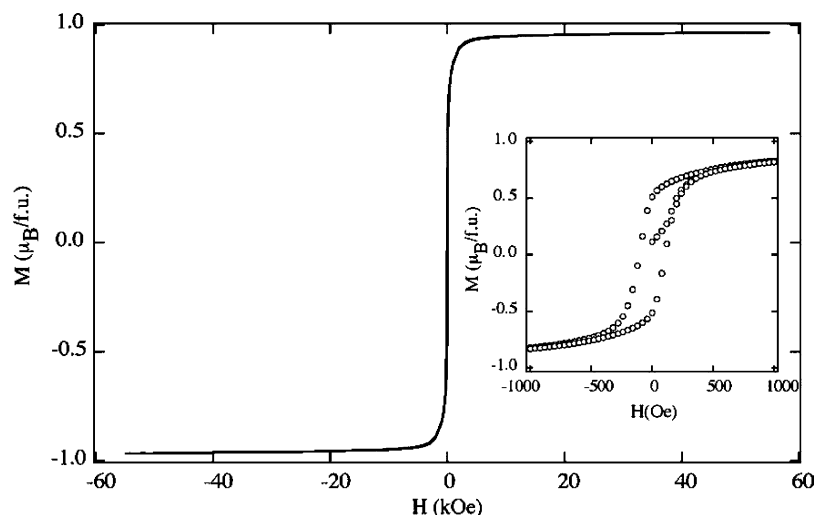


Fig. 5. The magnetization curve at 5 K of the Ca-containing phase. The inset is the enlargement of the low-magnetic-field part.

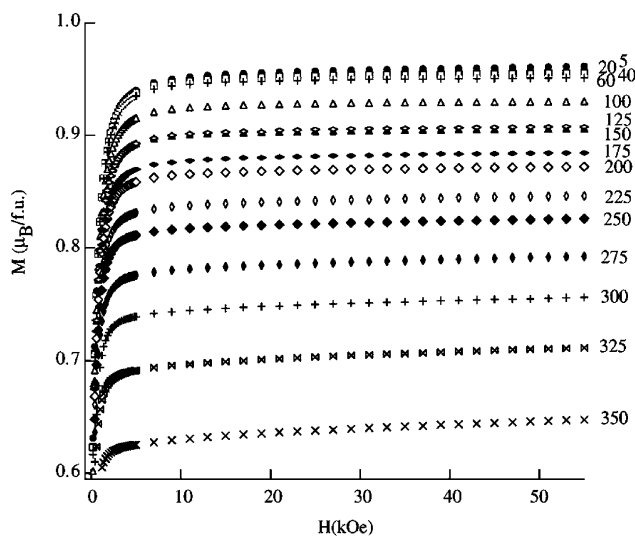


Fig. 6. The magnetization curves at various temperatures of the Ca-containing phase. The numbers shown indicate measuring temperatures in K.

present transition temperature of 440 K is unusually high in cuprates.

Electric resistivity of the Ca-containing sample was several Ω cm at room temperature and it increased very steeply with decreasing temperature. Assuming a localized electron system and based on the stoichiometric composition of $\text{Sr}_8\text{CaRe}_3\text{Cu}_4\text{O}_{24}$, B-site cation combinations may be $(3\text{Re}^{6+}, 4\text{Cu}^{3+}, \text{Ca}^{2+})$ or $(3\text{Re}^{7+}, \text{Cu}^{3+}, 3\text{Cu}^{2+}, \text{Ca}^{2+})$, where both Re^{6+} and Cu^{2+} are $S=1/2$ ions with $5d^1$ and $3d^9$, respectively. In either case, three spin $1/2$ ions should be present in the unit cell.

Experimentally, it was found that the oxygen content of a sample affects drastically the ferromagnetism. For instance, we made a sample with a nominal composition of $\text{Sr}(\text{Ca}_{0.125}\text{Re}_{0.375}\text{Cu}_{0.5})\text{O}_{2.75}$, i.e., the oxygen content

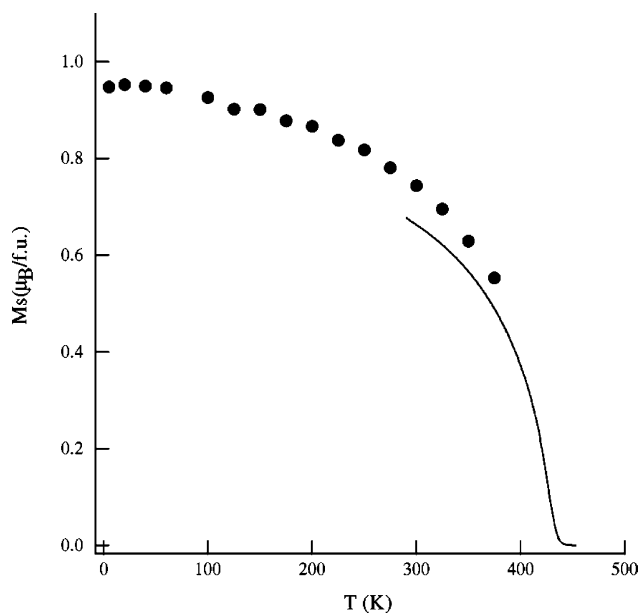


Fig. 7. Spontaneous magnetization M_s of the Ca-containing phase. The solid line indicates high-temperature-magnetization data at 1 kOe measured by VSM.

was decreased expecting a hole-free system with Re^{6+} and Cu^{2+} . The sample thus prepared was not ferromagnetic but paramagnetic down to 5 K. A similar result was obtained on the Ca-free system; as an example, the $\text{Sr}_{1.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_3$ sample (its XRD pattern is shown in Fig. 1) was paramagnetic down to 5 K whereas an oxygen-rich sample with $\text{Sr}_{1.15}\text{Re}_{0.35}\text{Cu}_{0.5}\text{O}_{3.2}$ showed ferromagnetism at room temperature. For the appearance of ferromagnetism, doping of holes and their ordered localization seem to be indispensable.

To consider the magnetic structure, it may be worth noting that the Cu2 sites form a network of

corner-shared octahedra (see Fig. 3) and geometric frustration is expected if the $S=1/2$ moments are located at the Cu2 sites and they are antiferromagnetically coupled. On the other hand, $M_0=3\mu_B$ is expected for a ferromagnetic coupling whose value is three times larger than the observed one. Topologically, the same configuration on the magnetic moments is derived when the $S=1/2$ moments are assumed to be at the Re sites (i.e., Re^{6+}). In either case, three $S=1/2$ moments alone do not give a magnetic structure with $M_0=1\mu_B$. According to Shannon's ionic radii [12], it is likely that the Cu2 sites are occupied by Cu^{2+} and the Cu1 sites by Cu^{3+} from the Cu–O bond lengths in Table 2, if the (3Re^{7+} , Cu^{3+} , 3Cu^{2+} , Ca^{2+}) configuration is the case. Then, a ferrimagnetic structure which gives $M_0=1\mu_B$ may be derived by assuming high spin state of Cu^{3+} ($S=1$) at the Cu1 site and Cu^{2+} ($S=1/2$) at the Cu2 site and an antiferromagnetic correlation between them.

However, we cannot rule out the (3Re^{6+} , 4Cu^{3+} , Ca^{2+}) configuration or other configuration which results from the deviation of composition from the stoichiometric one. NMR, neutron diffraction, electron energy loss spectroscopy (EELS) and band structure calculation studies are in progress. We need to wait their results for further consideration of the magnetic structure.

4. Conclusion

New phases $\text{Sr}_8A\text{Re}_3\text{Cu}_4\text{O}_{24}$ ($A=\text{Sr},\text{Ca}$) were discovered under high-pressure/high-temperature condition of 6 GPa and 1300–1350°C. Rietveld analysis of X-ray powder diffraction for the Ca-containing phase indicated an ordered perovskite-type structure with a cubic lattice of $\sim 8\text{Å}$. The unit cell contains eight perovskite-like blocks and their A -sites are occupied by Sr

exclusively. Three metals of Ca(Sr), Re and Cu are located at the B -sites in an ordered way. When these phases were prepared under high-oxygen-pressure condition, they showed ferromagnetism at room temperature. The Ca-containing phase had a unusually high T_C of 440 K as a cuprate, with a spontaneous magnetization of $\sim 1\mu_B/\text{f.u.}$

Acknowledgments

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