



# Article Dielectric and Spin-Glass Magnetic Properties of the A-Site Columnar-Ordered Quadruple Perovskite Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub>

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**Abstract:** Perovskite-type ABO<sub>3</sub> oxides show a number of cation-ordered structures, which have significant effects on their properties. The rock-salt-type order is dominant for B cations, and the layered order for A cations. In this work, we prepared a new perovskite-type oxide,  $Sm_2CuMn(MnTi_3)O_{12}$ , with a rare columnar A-site order using a high-pressure, high-temperature method at about 6 GPa and about 1700 K. Its crystal structure was studied with synchrotron powder X-ray diffraction. The compound crystallizes in space group  $P4_2/nmc$  (No. 137) at room temperature with a = 7.53477 Å and c = 7.69788 Å. The magnetic properties of the compound were studied with dc and ac magnetic susceptibility measurements and specific heat. Spin-glass (SG) magnetic properties were found with  $T_{SG} = 7$  K, while specific heat, in the form of  $C_p/T$ , showed a strong, very broad anomaly developing below 20 K and peaking at 4 K. The dielectric constant of  $Sm_2CuMn(MnTi_3)O_{12}$  was nearly frequency and temperature independent between 8 K and 200 K, with a value of about 50.  $Cu^{2+}$  doping drastically modified the magnetic and dielectric properties of  $Sm_2CuMn(MnTi_3)O_{12}$  in comparison with the parent compound  $Sm_2MnMn(MnTi_3)O_{12}$ , which showed a long-range ferrimagnetic order at 34–40 K. The antisite disorder of  $Cu^{2+}$  and  $Mn^{2+}$  cations between square-planar and octahedral sites was responsible for the SG magnetic properties of  $Sm_2CuMn(MnTi_3)O_{12}$ .

**Keywords:** quadruple perovskites; A-site columnar-ordered; antisite disorder; crystal structures; spin-glass

## 1. Introduction

The properties of the perovskite-structure oxide material, ABO<sub>3</sub>, are controlled by their chemical compositions and degrees of cation orderings [1,2]. There are perovskites with B-site cation orderings, A-site cation orderings, and both types of orderings. In the case of B-site ordering, the rock-salt-type order is dominant [3]. In the case of A-site ordering in ABO<sub>3</sub>, the layered-type order is dominant [1,2,4], but there are other types of ordering [5,6]. There are also two special families of perovskites with A-site orderings: A-site-ordered quadruple perovskites,  $AA'_{3}B_{4}O_{12}$  [7–9], and A-site columnar-ordered quadruple perovskites,  $A_{2}A'A''B_{4}O_{12}$  [10]. Quadruple perovskites can have ordered arrangements of 3*d* transition metals at the A (in general) perovskite sites in addition to the B sites. The resulting B–B, A–B, and A–A exchange interactions can produce complex interaction patterns and frustration networks and result in competing magnetic ground states, a large number of magnetic transitions and unexpected magnetism [11].

With A = R = rare earth elements and Bi and A' = A'' = B = Mn, interesting classes of perovskite manganites are formed, namely  $RMn_7O_{12}$  [9] and  $RMn_3O_6$  (in a short formula) [12]. They show several magnetic transitions with spin reorientations [9], and some



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). members have incommensurate magnetic structures [13]. The Cu<sup>2+</sup> doping of RMn<sub>7</sub>O<sub>12</sub> and RMn<sub>3</sub>O<sub>6</sub> has beneficial effects on their magnetic properties. in a sense that magnetic transition temperatures significantly increase, e.g., from about 80–87 K in RMn<sub>7</sub>O<sub>12</sub> [13] to 360–400 K in RCu<sub>3</sub>Mn<sub>3</sub>O<sub>12</sub> [14], and from about 60–77 K in RMn<sub>3</sub>O<sub>6</sub> [12] to 160–180 K in R<sub>2</sub>CuMnMn<sub>4</sub>O<sub>12</sub> [11,15]. In case of BiMn<sub>7</sub>O<sub>12</sub> [9], Cu<sup>2+</sup> doping results in complex structural behavior [16–18], complex magnetic behavior, and almost a linear rise of magnetic transition temperatures in BiCu<sub>x</sub>Mn<sub>7-x</sub>O<sub>12</sub> [18] for  $0.8 \le x \le 3$  from about 30 K (for 0 < x < 0.8) to 360 K for x = 3 [19]. The beneficial effects of Cu<sup>2+</sup> doping also took place in Y<sub>2</sub>MnGaMn<sub>4</sub>O<sub>12</sub>, which shows spin-glass magnetic properties at 26 K [20], as Y<sub>2</sub>CuGaMn<sub>4</sub>O<sub>12</sub> exhibits long-range ferrimagnetic ordering at 115 K [21].

Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> is a member of the A-site columnar-ordered quadruple perovskites. The magnetic properties of Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> [22,23] were somewhat unexpected, as it shows a long-range ferrimagnetic ordering with  $T_{\rm C}$  = 34–40 K and a welldefined M–H hysteresis loop with remnant magnetization of 2.3–2.4 µ<sub>B</sub>/f.u. at 5 K. The concentration of 3*d* transition metals (Mn<sup>2+</sup>) at the B sites (25%) was below the percolation limit for the corner-shared octahedral network. Nevertheless, Mn<sup>2+</sup> cations at the B sites were involved in the long-range ordering with a noticeable ordered magnetic moment [23]. Similar compounds without magnetic cations at the B sites (e.g., Ca<sub>2</sub>MnMnTi<sub>4</sub>O<sub>12</sub> [24] and NaRMnMnTi<sub>4</sub>O<sub>12</sub> [25]) show antiferromagnetic (AFM) transitions at lower temperatures of about 12 K. Therefore, there should be a noticeable involvement of the A–A and A–B exchange interactions in Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> to stabilize the ferrimagnetic structure out of AFM one and to increase the magnetic transition temperature. In addition, Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> was the first example among A-site columnar-ordered quadruple perovskites, demonstrating relaxor-type dielectric properties with broad maxima on the temperature dependence of a dielectric constant near 220 K [22].

In this work, we investigated the effects of  $Cu^{2+}$  doping on the magnetic and dielectric properties of the parent  $Sm_2MnMn(MnTi_3)O_{12}$  compound and prepared  $Sm_2CuMn(MnTi_3)O_{12}$  using a high-pressure, high-temperature method. However, in this case, the magnetic properties of the parent compound were "degraded" by  $Cu^{2+}$  doping, as only spin-glass (SG) magnetic properties were observed below  $T_{SG} = 7$  K. We attributed this degradation to antisite disorder. The relaxor-type dielectric properties of the parent compound disappeared, and  $Sm_2CuMn(MnTi_3)O_{12}$  demonstrated a frequency and temperature independent dielectric constant between 10 K and 200 K, with a value of about 50.

## 2. Experimental

 $Sm_2CuMn(MnTi_3)O_{12}$  was prepared using a high-pressure, high-temperature method using a belt-type high-pressure machine at 6 GPa and about 1700 K for 2 h in a Pt capsule. After annealing at 1700 K, the samples were quenched to room temperature (RT) by turning off the heating current, and the pressure was slowly released. Stoichiometric amounts of  $Sm_2O_3$  (99.9%), CuO (99.9%), MnO (99.99%), and TiO<sub>2</sub> (99.9%) were used as an initial oxide mixture with the 1:1:2:3 ratio, respectively. Commercial  $Sm_2O_3$ , CuO, and TiO<sub>2</sub> chemicals were used. A single-phase MnO oxide was prepared from a commercial  $MnO_2$  chemical by annealing at 1273 K for 4 h in a 20% H<sub>2</sub> + 80% Ar gas flow.

X-ray powder diffraction (XRPD) data were collected at RT with a RIGAKU Mini-Flex600 diffractometer (CuK $\alpha$  radiation; a 2 $\theta$  range of 8–100°; a step of 0.02°, and scan speed of 1°/min). The synchrotron XRPD data were collected at RT on the BL15XU beamline (the former NIMS beamline) of SPring-8 [26] between 2.04° and 60.23° at 0.003° intervals in 2 $\theta$  with a wavelength of  $\lambda$  = 0.65298 Å. The data between 6° and 60.23° were used in the refinements as no reflections were observed and expected below 6°. The sample was inserted into a Lindemann glass capillary tube (inner diameter: 0.1 mm), which was rotated during the measurements. The Rietveld analysis of all XRPD data was performed using the *RIETAN-2000* program [27].

Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) spectra were obtained on a Hitachi Miniscope TM3000 (operating at 15 kV). SQUID magnetometers (Quantum Design, MPMS-XL-7T and MPMS3) were used for the magnetic measurements. Temperature dependence was measured between 2 and 400 K in applied fields of 100 Oe and 10 kOe under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions on an MPMS-XL-7T. Magnetic-field dependence was measured at T = 2 K and 5 K between -70 and 70 kOe on MPMS3. Frequency dependent alternating current (ac) susceptibility measurements were performed on cooling with a Quantum Design MPMS3 instrument at different frequencies (*f*), different applied oscillating magnetic fields ( $H_{ac}$ ), and different static dc field ( $H_{dc}$ ). Relaxation curves were measured on MPMS3 using the following procedure: the sample was cooled down from 50 K to a measurement temperature at zero magnetic field, then a magnetic field of 100 Oe was applied, and magnetization was measured (as one scan within 2 s) as a function of time every 5 s.

Specific heat,  $C_p$ , was measured by cooling from 270 K to 2 K at zero magnetic field and from 150 K to 2 K at magnetic field of 90 kOe by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS).

The dielectric constant and dielectric loss were measured on a NOVOCONTROL Alpha-A High Performance Frequency Analyzer in a frequency range from 100 Hz to 665 kHz in a temperature range from 8 K to 330 K (on heating) at zero magnetic field.

## 3. Results and Discussion

The as-synthesized Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> contained a small amount of CuO impurity. In addition, the synchrotron XRPD pattern showed the presence of Pt impurity. However, Pt appeared from Pt capsules used in the synthesis and can be considered as an extrinsic impurity. The presence of a CuO impurity suggests that the main phase should be slightly Cu-deficient in comparison with the target composition. The morphology of the sample is shown in Figure 1. The particle sizes varied between about 10 and 50  $\mu$ m. The Ti:Mn:Sm:Cu cation ratio determined with EDX was 3.24(8):2.02(5):1.96(4):0.77(7), respectively. These values were close to the nominal values within  $3\sigma$ .





**Figure 1.** Scanning electron microscopy (SEM) images of the fractured surface of the as-synthesized  $Sm_2CuMn(MnTi_3)O_{12}$  sample. The scale bars are 100 µm (**left**) and 30 µm (**right**); magnification is 1000 (**left**) and 2000 (**right**). The surface is partially polished in the right panel. No polishing has been done in the left panel.

All of the reflections on the laboratory and synchrotron XRPD patterns (except CuO and Pt) could be indexed in a tetragonal system in space group  $P4_2/nmc$  (No. 137) (Figure 2). Sm<sub>2</sub>CuMnMnTi<sub>3</sub>O<sub>12</sub> was found to crystallize in the parent structure of the A-site columnar-ordered quadruple perovskites,  $A_2A'A''B_4O_{12}$  [10]. Therefore, the structural data for the parent compound Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> [22,23] were taken as an initial starting model.



**Figure 2.** Laboratory powder X-ray diffraction pattern of  $\text{Sm}_2\text{CuMn}(\text{MnTi}_3)\text{O}_{12}$  in a 2 $\theta$  range from 14° to 60.5°. Possible Bragg reflection positions for  $\text{Sm}_2\text{CuMn}(\text{MnTi}_3)\text{O}_{12}$  (the first row) and CuO impurities (the second row) are shown. The (*hkl*) indices of all of the observed reflections of  $\text{Sm}_2\text{CuMn}(\text{MnTi}_3)\text{O}_{12}$  are given.

In the structural analysis, we first assumed ideal cation distributions (that is, Sm at the A site, Cu at the square-planar A' site, Mn at the tetrahedral A'' site, and 0.75Ti + 0.25Mn at the octahedral B site) and refined the occupation factors (*g*) together with all of the other structural and nonstructural parameters (except *g*(B): one cation occupation factor should always be fixed to avoid significant correlations among the refined *g* parameters). In addition, in the structural analysis, we always assumed that Ti<sup>4+</sup> cations were located at the B site, as Ti<sup>4+</sup> cations strongly prefer octahedral sites [28].

The refined *g* values were as follows: g(Sm-A) = 0.9167(16), g(Cu-A') = 0.914(7), and g(Mn-A'') = 1.047(7). These values suggest that the ideal cation distribution was not realized, and there were some antisite disorders. The g(Cu-A') value suggested that this site should contain lighter elements that could only be Mn (with the above assumption on Ti). When only Mn was placed at the square-planar A' site, the occupation factor was g(Mn-A') = 1.112(8), meaning that heavier elements should also be at this site. Because it was difficult to precisely refine the distribution of Mn and Cu with X-ray diffraction, we introduced a virtual atom: MC = 0.5Mn + 0.5Cu. The precise distribution of Mn and Cu could only be determined with neutron diffraction. The disordering of cations at the Cu site was also observed as in many cases of such perovskites [21,22,25,29].

The refined structural parameters and primary bond lengths and angles in  $Sm_2CuMn(MnTi_3)O_{12}$  are listed in Tables 1 and 2. The experimental, calculated, and difference synchrotron patterns are shown in Figure 3. The crystal structure of  $Sm_2CuMn(MnTi_3)O_{12}$  is illustrated in the inset of Figure 3.

Crystal system	Tetragonal		
Space group	$P4_2/nmc$ (No. 137, cell choice 2)		
Z	2		
Caclulated density (g/cm <sup>3</sup> )	6.15		
Formula weight (g/cm <sup>3</sup> )	809.737		
Used <i>d</i> range (Å)	0.6507-6.238		
a (Å)	7.53477(1)		
c (Å)	7.69788(1)		
V (Å <sup>3</sup> )	437.0301(8)		
g(Sm)	0.9413(9)Sm + 0.0587Mn		
z(Sm)	0.22194(4)		
<i>B</i> (Sm) (Å <sup>2</sup> )	0.796(7)		
g(Cu)	0.4597MC + 0.0403Sm		
z(Cu)	0.7804(3)		
B(Cu) (Å <sup>2</sup> )	1.25(7)		
g(Mn)	0.963(3)Mn + 0.037Sm		
B(Mn) (Å <sup>2</sup> )	0.38(6)		
g(Ti)	0.25MC + 0.75Ti		
B(Ti) (Å <sup>2</sup> )	0.400(9)		
<i>y</i> (O1)	0.0571(3)		
z(O1)	-0.0379(3)		
B(O1) (Å <sup>2</sup> )	0.33(5)		
<i>y</i> (O2)	0.5363(3)		
z(O2)	0.5745(3)		
B(O2) (Å <sup>2</sup> )	0.36(5)		
<i>x</i> (O3)	0.44161(23)		
B(O3) (Å <sup>2</sup> )	1.48(7)		
R <sub>wp</sub> (%)	3.16		
R <sub>p</sub> (%)	2.17		
<i>R</i> <sub>I</sub> (%)	2.63		
R <sub>F</sub> (%)	1.69		

**Table 1.** Structure parameters of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> from synchrotron powder diffraction data ( $\lambda = 0.65298$  Å) at room temperature.

The Sm site is in the 4*d* site (0.25, 0.25, *z*); Cu is in the 4*c* site (0.75, 0.25, *z*); Mn is in the 2*b* site (0.75, 0.25, 0.25); Ti is in the 8*e* site (0, 0, 0); O1 and O2 are in the 8*g* site (0.25, *y*, *z*), and O3 is in the 8*f* site (x, -x, 0.25). *g* is the occupation factor. *g*(O1) = 1, *g*(O2) = 1, and *g*(O3) = 1. MC is a virtual atom: 0.5Mn + 0.5Cu.

**Table 2.** Bond lengths (in Å), bond angles (in deg), and distortion parameters of  $TiO_6$  ( $\Delta$ ) in  $Sm_2CuMn(MnTi_3)O_{12}$  at room temperature.

Sm-O1 × 2	2.352(3)
Sm–O1 $\times$ 2	2.472(2)
$Sm-O2 \times 2$	2.437(2)
Sm–O3 $ imes$ 4	2.744(1)
Cu-O3  imes 4	2.055(2)
Mn–O2 $\times$ 4	2.102(3)
$Ti-O1 \times 2$	1.954(1)
$Ti-O2 \times 2$	1.988(1)
$Ti-O3 \times 2$	2.023(1)
$\Delta(\text{TiO}_6)$	$2.0 imes10^{-4}$
Ti–O1–Ti $ imes$ 2	149.17(9)
Ti–O2–Ti $ imes$ 2	142.75(9)
Ti–O3–Ti × 2	144.17(9)



**Figure 3.** Full experimental (black crosses), calculated (red line), and difference (blue line at the bottom) room-temperature synchrotron powder X-ray diffraction patterns of  $\text{Sm}_2\text{CuMn}(\text{MnTi}_3)\text{O}_{12}$  in a  $2\theta$  range of  $6^\circ$  and  $60^\circ$ . The brown tick marks show possible Bragg reflection positions for the main phase, the blue tick marks are for CuO impurity (2.0 wt.%), and the green ones are for Pt impurity (0.3 wt.%). The inset shows a tetragonal crystal structure of  $\text{Sm}_2\text{CuMn}(\text{MnTi}_3)\text{O}_{12}$ ; TiO<sub>6</sub> octahedra (gray), MnO<sub>4</sub> tetrahedra (green), and ideal CuO<sub>4</sub> square-planar units (red) are plotted; Sm atoms are given by black circles; split Cu sites are shown by yellow circles.

Our model suggested that a small fraction of  $Cu^{2+}$  cations should be located at the B site. Indirect evidence for the location of  $Cu^{2+}$  cations at the octahedral site can be seen from the resulting Ti/MC–O bond lengths. In the parent and related compounds,  $R_2MnMn(MnTi_3)O_{12}$  (R = Nd, Sm, Eu, and Gd), the Ti/Mn–O bond lengths were about 1.99, 2.01, and 2.01 Å (from both the synchrotron [22,29] and neutron [23] diffraction data), resulting in an octahedral distortion parameter,  $\Delta$ , of about 0.2 × 10<sup>-4</sup>. On the other hand, in Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub>, the Ti/MC–O bond lengths were about 1.95, 1.99, and 2.02 Å resulting in  $\Delta$  of about 2.0 × 10<sup>-4</sup>. This rise in the octahedral distortion could be caused by the presence of a small amount of Jahn–Teller active Cu<sup>2+</sup> cations at this site.

Magnetic susceptibility curves,  $\chi$  versus *T*, of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> under applied magnetic fields of 0.1 kOe and 10 kOe are shown on Figure 4. There was a divergence between the 100 Oe ZFC and FCC curves at 7 K and a relatively sharp maximum on the 100 Oe ZFC curve at 7 K. A divergence between the ZFC and FCC curves almost disappeared under 10 kOe. These features are typical for spin-glass transitions [30–32]. Isothermal magnetization, *M* versus *H*, curves demonstrated an extended S-type shape with very weak and narrow hysteresis (Figure 5). Almost no hysteresis was observed at 5 K because 5 K was close to its  $T_{SG} = 7$  K; on the other hand, the hysteresis was noticeably wider at a lower temperature of 2 K. Such *M* versus *H* curves are also typical for spin glasses [30–32].



**Figure 4.** The left-hand axis shows the ZFC (filled symbols) and FCC (empty symbols) dc magnetic susceptibility curves ( $\chi = M/H$ ) of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> at 100 Oe (black) and 10 kOe (red). The right-hand axis gives the 10 kOe FCC  $\chi^{-1}$  versus *T* curve with the Curie–Weiss fit between 250 K and 345 K (black line). Parameters of the fits are shown on the figure. The inset shows details below 30 K.



**Figure 5.** *M* versus *H* curves of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> at T = 2 K (black) and T = 5 K (red) (f.u.: formula unit). The inset shows details near the origin. Parameters of the *M* versus *H* curve at T = 2 K are given:  $M_S$  is the magnetization value at H = 70 kOe,  $M_R$  is the remnant magnetization, and  $H_C$  is the coercive field.

The inverse magnetic susceptibilities ( $\chi^{-1}$  versus *T*) followed the Curie–Weiss law at high temperatures (Figure 4). To obtain the effective magnetic moment and the Curie–Weiss temperature, we performed fits between 250 and 345 K using the 10 kOe FCC

curves (the fit and fitting parameters are summarized on Figure 4). The experimental effective magnetic moment was close to the expected one (8.803  $\mu_B$ ; in the calculations we used 1.5  $\mu_B$  for Sm<sup>3+</sup> [33]). The negative Curie–Weiss temperature shows that the main magnetic interactions were antiferromagnetic in nature. The ratio between the Curie–Weiss temperature (-81.5 K) and  $T_{SG}$  (the so-called frustration ratio) was about 11, indicating a strong degree of magnetic frustration. We note that CuO was in an antiferromagnet with transition temperatures of 213 K and 230 K. Therefore, CuO impurity should not affect the reported magnetic properties at low temperatures.

To confirm the spin-glass nature of the sample, we measured ac magnetic susceptibility curves (Figures 6 and 7). We note that no dependence of the  $\chi'$  and  $\chi''$  values on the applied  $H_{ac}$  field was observed (inset of Figure 6). We indeed observed typical features of spin-glasses: peak positions were frequency-dependent and shifted to higher temperatures with increasing frequency; in addition, peak intensity was suppressed on the  $\chi'$  versus *T* curves and enhanced on the  $\chi''$  versus *T* curves with increasing frequency. All of these features are typical for spin glasses [30–32]. In addition, the shape of the  $\chi'$  versus *T* and the  $\chi''$  versus *T* curves was also typical for spin glasses. The criterion, which quantifies the relative change of the spin-glass temperature per frequency decade and is defined as  $\Delta T_{SG}/[T_{SG}\Delta \log(f)]$ , was about 0.023 for Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> (with  $T_{SG} = 7.2$  K at f = 2 Hz and  $T_{SG} = 7.6$  K at f = 500 Hz). This value is often observed in different spin-glass materials [30–32].

Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> shows time-dependent magnetic properties below  $T_{SG}$ , namely magnetization relaxation (Figure 8). Above  $T_{SG}$ , no noticeable relaxation of magnetization was detected. Time-dependent magnetic properties, such as relaxation, are typical features of spin-glass systems. Relaxation below  $T_{SG}$  was fitted by the stretched exponential function,  $f(t) = M_0 - M_{SG} \times \exp[-(t/t_r)^\beta]$  [30], and the resultant parameters are listed on Table 3. The most important parameter is the mean relaxation time,  $t_r$ , and it decreases monotonically with increasing temperature.

**Table 3.** Results of the fittings of the relaxation curves of  $Sm_2CuMn(MnTi_3)O_{12}$  at different temperatures.

<i>T</i> (K)	$M_0$	$M_{ m SG}$	$t_r$ (s)	β
2	22.80(13)	23.67(18)	1270(24)	0.4362(4)
3	26.01(12)	27.20(20)	979(16)	0.4461(4)
4	22.81(10)	23.94(18)	800(11)	0.4495(4)
5	17.74(6)	18.62(13)	671(8)	0.4558(4)
6	12.34(14)	13.01(9)	554(6)	0.4654(4)

The fitting equation is  $f(t) = M_0 - M_{SG} \times \exp[-(t/t_r)^{\beta}]$  [30] applied to the  $100 \times [M(t) - M(0)]/M(0)$  versus time (*t*) curves.

The specific heat data showed a noticeable magnetic contribution to the total specific heat below about 20 K, where it could be clearly seen as a rise in  $C_p/T$  values below 20 K (Figure 9). No  $\lambda$ -type anomaly was detected in the  $C_p$  versus *T* curve (inset of Figure 9, a green curve). Instead, a broad anomaly was seen in the  $C_p$  versus *T* curve, which gave a broad peak centered at 4 K in the  $C_p/T$  versus *T* curve. Therefore, specific heat measurements confirmed the absence of long-range magnetic ordering. A magnetic field of 90 kOe slightly suppressed the peak near 4 K and moved the magnetic entropy into the 14–40 K range.



**Figure 6.** (a) Real ( $\chi'$ ) and (b) imaginary ( $\chi''$ ) parts of the ac magnetic susceptibility curves of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> at different frequencies. The insets in (**a**,**b**) show the  $\chi'$  versus *T* and  $\chi''$  versus *T* curves at different  $H_{ac} = 0.05$ , 0.5, and 5 Oe and one frequency (f = 300 Hz) (the  $\chi''$  data at  $H_{ac} = 0.05$  Oe are not shown because they were too noisy).



**Figure 7.** (**a**–**d**)  $\chi'$  versus *T* curves of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> at *f* = 2 Hz and 500 Hz and different bias dc fields: (**a**)  $H_{dc} = 0$  Oe, (**b**) 100 Oe, (**c**) 1 kOe, and (**d**) 10 kOe. Insets show  $\chi''$  versus *T* curves (the  $\chi''$  data at *f* = 2 Hz and  $H_{dc} = 10$  kOe were too noisy and not shown). (**e**) All  $\chi'$  versus *T* curves at *f* = 500 Hz are shown in one figure. (**f**) All  $\chi''$  versus *T* curves at *f* = 500 Hz are shown in one figure.

The temperature dependence of the dielectric constant and dielectric loss is shown in Figure 10. The dielectric constant was nearly temperature and frequency-independent between 8 and 200 K. Above about 200 K, a sharp rise in the dielectric constant was observed, where the magnitude of the rise depended on frequency. This behavior typically originates from the Maxwell–Wagner contribution due to increased conductivity. No broad anomalies were observed in Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> in comparison with the parent compound Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub>. This fact shows that Cu<sup>2+</sup> doping drastically modified the dielectric properties as well, in addition to the magnetic properties. We note that Pt impurity was only observed in a powder sample, which could contain parts from the



surface. The surfaces of a pellet used for dielectric measurements were polished. Therefore, Pt impurity should not present in a pellet and affect dielectric measurements.

**Figure 8.** Relaxation curves defined as  $100 \times [M(t) - M(0)]/M(0)$  versus time (*t*) for Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> at temperatures of 2, 3, 4, 5, 6, 7, and 10 K. Experimental points are given by symbols, and the red line shows the fit at 3 K as an example. The equation used for fitting and the resultant parameters are listed in Table 3.



**Figure 9.** (a)  $C_p/T$  versus *T* curves of Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> at H = 0 Oe (red triangles) and 90 kOe (blue triangles) in comparison with the parent compound Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> at H = 0 Oe (black circles) and 90 kOe (brown circles).  $C_p$  is the total specific heat. The arrows show the positions of the magnetic anomalies. The inset shows the  $C_p/T$  versus *T* curve at H = 0 Oe below 30 K, and the  $C_p$  versus *T* curve at H = 0 Oe (green circles). For the  $C_p$  versus *T* curve, the  $C_p$  values were divided by 20, and the  $C_p$  unit is J K<sup>-1</sup> mol<sup>-1</sup>. (b) Comparison of  $C_p/T$  versus *T* data for Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> (red triangles) and Sm<sub>2</sub>MnZn(MnTi<sub>3</sub>)O<sub>12</sub> (black circles) [34] at H = 0 Oe.



Figure 10. Temperature dependence of the dielectric constant at different frequencies in  $Sm_2CuMn(MnTi_3)O_{12}$ . The inset shows temperature dependence of dielectric loss in the logarithmic scale.

Spin-glass magnetic properties were also observed in Sm<sub>2</sub>MnZn(MnTi<sub>3</sub>)O<sub>12</sub> at  $T_{SG}$  = 6.5 K, with a significant antisite disorder [34]. This fact shows that antisite structural disorder should play a major role in the modification of magnetic properties of the parent Sm<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> compound, not the nature of dopant cations (magnetic as Cu<sup>2+</sup> or non-magnetic as Zn<sup>2+</sup>). Both Sm<sub>2</sub>CuMn(MnTi<sub>3</sub>)O<sub>12</sub> and Sm<sub>2</sub>MnZn(MnTi<sub>3</sub>)O<sub>12</sub> demonstrated similar low-temperature specific heat features (Figure 9b).

The beneficial effects of  $Cu^{2+}$  doping in  $RMn_7O_{12}$  [13,14],  $RMn_3O_6$  [11,12,15], and  $Y_2MnGaMn_4O_{12}$  [20,21] originate from the fact that  $Cu^{2+}$  doping is aliovalent doping, which produces  $Mn^{4+}$  cations. A mixture of  $Mn^{3+}$  and  $Mn^{4+}$  at the B sites of perovskites significantly enhanced the exchange interactions and magnetic transition temperatures. On the other hand,  $Cu^{2+}$  doping in the parent  $Sm_2MnMn(MnTi_3)O_{12}$  compound was isovalent doping. Such doping did not change the oxidation state of Mn, while the antisite disordering "degraded" the magnetic properties.

## 4. Conclusions

A new member of the A-site columnar-ordered quadruple perovskite family,  $Sm_2CuMn(MnTi_3)O_{12}$ , was prepared using a high-pressure, high-temperature method.  $Cu^{2+}$  doping significantly modified the properties of the parent  $Sm_2MnMn(MnTi_3)O_{12}$  compound, as spin-glass magnetic properties at  $T_{SG} = 7$  K were observed in  $Sm_2CuMn(MnTi_3)O_{12}$  in comparison with the long-range ferrimagnetic order at  $T_C = 34-40$  K in  $Sm_2MnMn(MnTi_3)O_{12}$ . In addition, relaxor-like dielectric properties of  $Sm_2MnMn(MnTi_3)O_{12}$  disappeared in  $Sm_2CuMn(MnTi_3)O_{12}$ , which showed a nearly temperature and frequency-independent dielectric constant between 8 and 200 K with a value of about 50.

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## References

- Abakumov, A.M.; Tsirlin, A.A.; Antipov, E.V. Transition-Metal Perovskites. In *Comprehensive Inorganic Chemistry II (Second Edition):* From Elements to Applications; Reedijk, J., Poeppelmeier, K.R., Eds.; Elsevier: Amsterdam, The Netherlands, 2013; Volume 2, pp. 1–40.
- 2. King, G.; Woodward, P.M. Cation ordering in perovskites. J. Mater. Chem. 2010, 20, 5785–5796. [CrossRef]
- 3. Vasala, S.; Karppinen, M. A<sub>2</sub>B'B''O<sub>6</sub> perovskites: A review. Prog. Solid State Chem. 2015, 43, 1–36. [CrossRef]
- Knapp, M.C.; Woodward, P.M. A-site cation ordering in AA'BB'O<sub>6</sub> perovskites. J. Solid State Chem. 2006, 179, 1076–1085. [CrossRef]
- Rubel, M.H.K.; Miura, A.; Takei, T.; Kumada, N.; Mozahar Ali, M.; Nagao, M.; Watauchi, S.; Tanaka, I.; Oka, K.; Azuma, M.; et al. Superconducting double perovskite bismuth oxide prepared by a low-temperature hydrothermal reaction. *Angew. Chem. Int. Ed.* 2014, 126, 3673–3677.
- 6. Rubel, M.H.K.; Takei, T.; Kumada, N.; Mozahar Ali, M.; Miura, A.; Tadanaga, K.; Oka, K.; Azuma, M.; Yashima, M.; Fujii, K.; et al. Hydrothermal synthesis, crystal structure, and superconductivity of a double-perovskite Bi oxide. *Chem. Mater.* **2016**, *28*, 459–465.
- 7. Vasil'ev, A.N.; Volkova, O.S. New functional materials AC<sub>3</sub>B<sub>4</sub>O<sub>12</sub> (review). Low Temp. Phys. 2007, 33, 895–914. [CrossRef]
- 8. Long, Y.W. A-site ordered quadruple perovskite oxides AA'<sub>3</sub>B<sub>4</sub>O<sub>12</sub>. Chin. Phys. B 2016, 25, 078108. [CrossRef]
- Belik, A.A.; Johnson, R.D.; Khalyavin, D.D. The rich physics of A-site-ordered quadruple perovskite manganites AMn<sub>7</sub>O<sub>12</sub>. Dalton Trans. 2021, 50, 15458–15472. [CrossRef]
- Belik, A.A. Rise of A-site columnar-ordered A<sub>2</sub>A'A"B<sub>4</sub>O<sub>12</sub> quadruple perovskites with intrinsic triple order. *Dalton Trans.* 2018, 47, 3209–3217. [CrossRef]
- 11. Vibhakar, A.M.; Khalyavin, D.D.; Manuel, P.; Liu, J.; Belik, A.A.; Johnson, R.D. Spontaneous rotation of ferrimagnetism driven by antiferromagnetic spin canting. *Phys. Rev. Lett.* **2020**, *124*, 127201.
- 12. Zhang, L.; Matsushita, Y.; Yamaura, K.; Belik, A.A. Five-fold ordering in high-pressure perovskites RMn<sub>3</sub>O<sub>6</sub> (R = Gd-Tm and Y). *Inorg. Chem.* **2017**, *56*, 5210–5218. [CrossRef] [PubMed]
- 13. Johnson, R.D.; Khalyavin, D.D.; Manuel, P.; Zhang, L.; Yamaura, K.; Belik, A.A. Magnetic structures of the rare-earth quadruple perovskite manganites *RMn*<sub>7</sub>O<sub>12</sub>. *Phys. Rev. B Condens. Matter Mater. Phys.* **2018**, *98*, 104423. [CrossRef]
- Sanchez-Benitez, J.; Alonso, J.A.; Martinez-Lope, M.J.; de Andres, A.; Fernandez-Diaz, M.T. Enhancement of the Curie temperature along the perovskite series RCu<sub>3</sub>Mn<sub>4</sub>O<sub>12</sub> driven by chemical pressure of R<sup>3+</sup> cations (R = rare earths). *Inorg. Chem.* 2010, 49, 5679–5685. [CrossRef] [PubMed]
- 15. Belik, A.A.; Khalyavin, D.D.; Zhang, L.; Matsushita, Y.; Katsuya, Y.; Tanaka, M.; Johnson, R.D.; Yamaura, K. Intrinsic triple order in A-site columnar-ordered quadruple perovskites: Proof of concept. *ChemPhysChem* **2018**, *19*, 2449–2452. [CrossRef]
- 16. Belik, A.A.; Matsushita, Y.; Khalyavin, D.D. Reentrant structural transitions and collapse of charge and orbital orders in quadruple perovskites. *Angew. Chem. Int. Ed.* **2017**, *56*, 10423–10427. [CrossRef]
- 17. Khalyavin, D.D.; Johnson, R.D.; Orlandi, F.; Radaelli, P.G.; Manuel, P.; Belik, A.A. Emergent helical texture of electric dipoles. *Science* 2020, *369*, 680–684. [CrossRef]
- 18. Belik, A.A.; Matsushita, Y.; Tanaka, M.; Johnson, R.D.; Khalyavin, D.D. A plethora of structural transitions, distortions and modulations in Cu-doped BiMn<sub>7</sub>O<sub>12</sub> quadruple perovskites. *J. Mater. Chem. C* **2021**, *9*, 10232–10242. [CrossRef]
- 19. Kayser, P.; Martinez-Lope, M.J.; Alonso, J.A.; Sanchez-Benitez, J.; Fernandez, M.T. High-pressure synthesis and characterization of BiCu<sub>3</sub>(Mn<sub>4-x</sub>Fe<sub>x</sub>)O<sub>12</sub> (*x* = 0, 1.0, 2.0) complex perovskites. *J. Solid State Chem.* **2013**, 204, 78–85. [CrossRef]
- 20. Liu, R.; Khalyavin, D.D.; Tsunoda, N.; Kumagai, Y.; Oba, F.; Katsuya, Y.; Tanaka, M.; Yamaura, K.; Belik, A.A. Spin-glass magnetic properties of A-site columnar-ordered quadruple perovskites  $Y_2$ MnGa(Mn<sub>4-x</sub>Ga<sub>x</sub>)O<sub>12</sub> with  $0 \le x \le 3$ . *Inorg. Chem.* **2019**, *58*, 14830–14841.
- 21. Belik, A.A.; Khalyavin, D.D.; Matsushita, Y.; Yamaura, K. Triple A-site cation ordering in the ferrimagnetic Y<sub>2</sub>CuGaMn<sub>4</sub>O<sub>12</sub> perovskite. *Inorg. Chem.* **2022**, *61*, 14428–14435. [CrossRef]
- 22. Belik, A.A.; Zhang, L.; Liu, R.; Khalyavin, D.D.; Katsuya, Y.; Tanaka, M.; Yamaura, K. Valence variations by B-site doping in A-site columnar-ordered quadruple perovskites  $Sm_2MnMn(Mn_{4-x}Ti_x)O_{12}$  with  $1 \le x \le 3$ . *Inorg. Chem.* **2019**, *58*, 3492–3501. [CrossRef]
- Vibhakar, A.M.; Khalyavin, D.D.; Manuel, P.; Liu, R.; Yamaura, K.; Belik, A.A.; Johnson, R.D. Effects of magnetic dilution in the ferrimagnetic columnar ordered Sm<sub>2</sub>MnMnMn<sub>4-x</sub>Ti<sub>x</sub>O<sub>12</sub> perovskites. *Phys. Rev. B Condens. Matter Mater. Phys.* 2020, 102, 214428. [CrossRef]

- Aimi, A.; Mori, D.; Hiraki, K.; Takahashi, T.; Shan, Y.J.; Shirako, Y.; Zhou, J.S.; Inaguma, Y. High-pressure synthesis of A-site ordered double perovskite CaMnTi<sub>2</sub>O<sub>6</sub> and ferroelectricity driven by coupling of A-site ordering and the second-order Jahn–Teller effect. *Chem. Mater.* 2014, 26, 2601–2608. [CrossRef]
- 25. Liu, R.; Scatena, R.; Khalyavin, D.D.; Johnson, R.D.; Inaguma, Y.; Tanaka, M.; Matsushita, Y.; Yamaura, K.; Belik, A.A. High-pressure synthesis, crystal structures, and properties of A-site columnar-ordered quadruple perovskites NaRMn<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> with R = Sm, Eu, Gd, Dy, Ho, Y. *Inorg. Chem.* 2020, *59*, 9065–9076. [CrossRef]
- 26. Tanaka, M.; Katsuya, Y.; Matsushita, Y.; Sakata, O. Development of a synchrotron powder diffractometer with a one-dimensional X-ray detector for analysis of advanced materials. *J. Ceram. Soc. Jpn.* **2013**, *121*, 287–290. [CrossRef]
- 27. Izumi, F.; Ikeda, T. A Rietveld-analysis program RIETAN-98 and its applications to zeolites. *Mater. Sci. Forum* **2000**, *321*, 198–205. [CrossRef]
- 28. Waroquiers, D.; Gonze, X.; Rignanese, G.-M.; Welker-Nieuwoudt, C.; Rosowski, F.; Gobel, M.; Schenk, S.; Degelmann, P.; André, R.; Glaum, R.; et al. Statistical analysis of coordination environments in oxides. *Chem. Mater.* **2017**, *29*, 8346–8360. [CrossRef]
- 29. Liu, R.; Tanaka, M.; Mori, H.; Inaguma, Y.; Yamaura, K.; Belik, A.A. Ferrimagnetic and relaxor ferroelectric properties of R<sub>2</sub>MnMn(MnTi<sub>3</sub>)O<sub>12</sub> perovskites with R = Nd, Eu, and Gd. *J. Mater. Chem.* C **2021**, *9*, 947–956. [CrossRef]
- 30. Mydosh, J.A. Spin Glass: An Experimental Introduction; Taylor & Francis: London, UK, 1993.
- 31. von Lohneysen, H. Low energy excitations in amorphous metals. Phys. Rep. 1981, 79, 161–212. [CrossRef]
- 32. Binder, K.; Young, A.P. Spin-glasses: Experimental facts, theoretical concepts, and open questions. *Rev. Mod. Phys.* **1986**, *58*, 801–976. [CrossRef]
- 33. Kittel, C. Introduction to Solid State Physics, 8th ed.; John Wiley and Sons, Inc.: New York, NY, USA, 2005.
- 34. Belik, A.A.; Liu, R.; Yamaura, K. Spin-glass to long-range order to spin-glass evolution of magnetic properties with the composition in Sm<sub>2</sub>MnZnMn<sub>4-x</sub>Ti<sub>x</sub>O<sub>12</sub> (*x* = 1, 2, and 3) perovskites. *J. Alloys Compd.* **2023**, *932*, 166297. [CrossRef]