

B-site ordered and disordered phases in A-site columnar-ordered quadruple perovskites $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$

Xuan Liang,^{a, b} Kazunari Yamaura,^{a, b} Alexei A. Belik^{a,*}

^aResearch Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan.

^bGraduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan.

Abstract

Solid solutions $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$, belonging to the A-site columnar-ordered quadruple perovskite subfamily $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ and prepared by a high-pressure, high-temperature method at about 6 GPa and about 1700 K, were investigated in a compositional range of $0.2 \leq x \leq 2.0$. Crystal structures were studied using synchrotron powder X-ray diffraction. Two regions with different cation orders in the B sublattice were found: a narrow region of $0.8 \leq x \leq 1.0$ had a B-site disordered structure with space group $P4_2/nmc$ (No. 137), and a wider region of $1.6 \leq x \leq 2.0$ had a B-site rock-salt-ordered structure with space group $P4_2/n$ (No. 86). Small anti-site disorder of Nd and Mn was detected among the A, A', and A'' sites. In the B-site rock-salt-ordered structures, one B site was solely occupied by Mn, the second B' site had a mixture of Sb and Mn (for $x < 2$). The samples showed complex magnetic behavior with two ferrimagnetic transitions. T_{C1} monotonically increased (from 66 K to 75 K) and T_{C2} was almost constant (about 6–7 K) for $0.8 \leq x \leq 1.0$. T_{C1} monotonically decreased (from 77 K to 63 K) and T_{C2} monotonically increased (from 19 K to 39 K) for $1.6 \leq x \leq 2.0$. There was evidence for the third magnetic transition in the $1.7 \leq x \leq 2.0$ samples, and T_{C3} increased from 13 K to 20 K with increasing x .

Keywords: A-site columnar-ordered; quadruple perovskites; ferrimagnets; high-pressure

* Corresponding author. E-mail address: Alexei.Belik@nims.go.jp (A.A. Belik).

1. Introduction

Perovskite-structure compounds have been identified as one of the most promising materials owing to their rich physical properties. They already have a wide range of applications, for example, in photovoltaics, catalysis, and other various devices [1–4]. The perovskite ABO_3 structure is built from a framework of corner-shared BO_6 octahedra that form cavities, which are filled with A cations. Depending on the size mismatch of A, B, and O, the BO_6 octahedral framework requires different distortions to stabilize the structure. One of such distortions is rigid BO_6 octahedral tilts, which can be described by the Glazer tilt system and B–O–B bond angles [5]. Different tilts give rise to diverse and distinct numbers and types of cavities for A cations. In the case of the most commonly observed tilt system of $a^-b^+a^-$ (written in the Glazer notation [5]), only one type of an A-site cavity is created; but the coordination number of A cations in ABO_3 perovskites can be reduced from 12 (for small tilts) to 8 (for large tilts). The $a^+a^+a^-$ tilt produces two types of cavities in the case of $\text{AA}'_3\text{B}_4\text{O}_{12}$ quadruple perovskites. The A site has a 12-fold coordination similar to the coordination number in the ideal undistorted ABO_3 structure, while the A' site has a square-planar coordination [6, 7]. Another special class of the perovskite family with the $a^+a^+c^-$ tilt system, $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$, has original columnar-type arrangements of three types of cavities: 10-coordinated A, 4-coordinated square-planar A', and 4-coordinated tetrahedral A'' sites [8]. In $\text{AA}'_3\text{B}_4\text{O}_{12}$ and $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ quadruple perovskites, the square-planar A' site is usually occupied by Jahn–Teller cations (such as Cu^{2+} and Mn^{3+}). However, other cations (such as Mn^{2+} , Co^{2+} , and Fe^{2+}) can also be incorporated using a high-pressure high-temperature preparation method [8].

To enhance and customize properties of perovskite-type materials, various combinations of A and B cations are frequently incorporated. The distribution of these cations within the A- and B-sites can either be random or result in ordered structures depending on characteristics of A and B cations, including their ionic radii, oxidation states, and electronic configurations. Since the coordination environment of the B cations in perovskites is fixed to octahedral, oxidation state differences are the main factor influencing the ordering of B-site cations. The large difference in the oxidation state of B and B' cations favors ordered distributions; B and B' cations are usually ordered when the charge difference is larger than 2 [9]. A lot of B-site-ordered $\text{A}_2\text{BB}'\text{O}_6$ double perovskites have been reported to date [10]. However, A-site-ordered $\text{AA}'\text{B}_2\text{O}_6$ double perovskites are significantly less common and are often achieved together with simultaneous 1:1 cation orders at both A- and B-sites, which are known as doubly ordered (or double double [11]) perovskites, $\text{AA}'\text{BB}'\text{O}_6$ [12, 13]. A-site-ordered structures can also be stabilized by octahedral tilts combined with large differences in size and electronic properties of A cations as in $\text{AA}'_3\text{B}_4\text{O}_{12}$ quadruple perovskites with 1:3 double A-site ordering and $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ quadruple perovskites with 2:1:1 triple A-site ordering [7, 8, 14]. Triple A-site ordering by different cations was found, for example, in $\text{Ho}_2\text{MnGa}(\text{Mn}_{4-x}\text{Ga}_x)\text{O}_{12}$ [14], $\text{Y}_2\text{MnGa}(\text{Mn}_{4-x}\text{Ga}_x)\text{O}_{12}$ [15], $\text{Y}_2\text{CuGaMn}_4\text{O}_{12}$ [16], and $\text{Dy}_2\text{CuZnMn}_4\text{O}_{12}$ [17]. However, in many cases, triple ordering in such perovskites is hidden because $\text{A}' = \text{A}''$.

Some perovskite materials can be synthesized in both cation-ordered structures and disordered structures resulting in significant alterations in their properties. For example, the ferromagnetic Curie temperature increased from 270 K in the disordered $\text{LaBaMn}_2\text{O}_6$ with colossal magnetoresistance to 335 K for the cation-ordered phase [18]. The gradual introduction of B-site disorder progressively overwhelmed the long-range ferrimagnetic ordering in Y_2CoIrO_6

sample with B-site ordering [19]. Noticeable changes of magnetic properties have also been reported in A-site-ordered and A-site-disordered modifications of the CaMnMnWO_6 perovskite [11]. Some $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ quadruple perovskites can also be prepared in different modifications depending on synthesis conditions, for example, polar and non-polar phases of $\text{NaYMn}_2\text{Ti}_4\text{O}_{12}$ were reported [20].

In this work, $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions were prepared at 6 GPa. They belong to the A-site columnar-ordered quadruple perovskite subfamily. Two regions with different cation orders in the B sublattice were found: the $0.8 \leq x \leq 1.0$ compositions had a B-site disordered structure while the $1.6 \leq x \leq 2.0$ compositions had a B-site rock-salt-ordered structure. Other compositions were multi-phase mixtures. Two magnetic transitions were found with systematic changes of phase transition temperatures as a function of the composition. There was evidence for the third magnetic transition in the $1.7 \leq x \leq 2.0$ compositional range. The $x = 2.0$ sample was prepared before at 10 GPa and investigated using neutron diffraction and magnetic measurements [21].

2. Experimental section

$\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ samples were prepared from stoichiometric mixtures of Nd_2O_3 (99.9%), Sb_2O_3 (99.9%), and Mn_2O_3 . Mn_2O_3 was prepared from commercial MnO_2 (99.99%) by heating in air at 920 K for 24 h. Nd_2O_3 was dried in air at 1270 K for 1 h and the other two oxides were dried in air at 390 K for 4 h before use. All $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ samples were synthesized at about 6 GPa and about 1700 K for 2 h in Pt capsules using a belt-type high-pressure machine. After annealing, the samples were cooled down to room temperature (RT) by turning off the heating current, and the pressure was slowly released.

X-ray powder diffraction (XRPD) data at RT were collected on a RIGAKU MiniFlex600 diffractometer using $\text{CuK}\alpha$ radiation at RT (in a 2θ range of $5\text{--}100^\circ$ with a step of 0.02° , and a scan speed of $3^\circ/\text{min}$). Synchrotron XRPD data were collected at RT on the BL02B2 beamline of SPring-8 at RT between 1.95° and 78.09° at a 0.006° interval in 2θ with the wavelength of $\lambda = 0.42019 \text{ \AA}$ [22]. The data up to 70° were used in the refinements as no experimental reflections were observed above 70° . The samples were placed into Lindemann glass capillary tubes (inner diameter: 0.2 mm), which were rotated during measurements. The Rietveld analysis of all XRPD data was performed using the *RIETAN-2000* program [23].

Magnetic measurements were performed on a SQUID magnetometer (Quantum Design, MPMS3) between 2 K and 150 K (or 300 K) in an applied magnetic field of 100 Oe and between 2 K and 400 K in an applied field of 10 kOe under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions. Isothermal magnetization measurements were performed between -70 and 70 kOe at 5 K, 25 K, 60 K, and 100 K. Specific heat was measured on a Quantum Design PPMS-9T instrument on cooling (and on heating in some cases) at magnetic fields of 0 Oe and 90 kOe.

3. Results and discussion

3.1. Phase compositions, crystal symmetries, and crystal structure refinements

XRPD patterns of all members of the $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions under $\text{CuK}\alpha$ radiation are shown in Fig. S1a–S1c. Our phase analysis showed that the $x = 0.2$ sample contained about 46.6 wt. % of a $P4_2/nmc$ phase, about 44.0 wt. % of a $\text{NdMn}_7\text{O}_{12}$ ($\text{AA}'_3\text{B}_4\text{O}_{12}$ -type

perovskite) phase, and about 9.4 wt. % of a NdMnO_3 -related (ABO_3 -type perovskite) phase. The NdMnO_3 -related phase disappeared in the $x = 0.4$ sample, and the amount of the $\text{NdMn}_7\text{O}_{12}$ phase also decreased with increasing the x value. The $x = 0.6$ sample contained 10.1 wt. % of the $\text{NdMn}_7\text{O}_{12}$ impurity, while the $x = 0.8$ sample contained traces of the $\text{NdMn}_7\text{O}_{12}$ impurity (2.3 wt. %) indicating that the $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions form from about $x = 0.8$. Samples with $x = 0.8, 0.9$, and 1.0 adopted the parent structure of the A-site columnar-ordered quadruple perovskite family with space group $P4_2/nmc$ which can be represented by SmMnGaTiO_6 , GdMnGaTiO_6 [24], and $\text{CaFeTi}_2\text{O}_6$ [25]. A characteristic reflection of the $P4_2/nmc$ structure near 33.2° (for $\text{CuK}\alpha$ radiation) was still observed in samples up to $x = 1.5$ (Fig. S1c). At the same time, a characteristic reflection of the $P4_2/n$ structure [due to B-site ordering, with the Miller index of (111)] near 19.8° (for $\text{CuK}\alpha$ radiation) appeared in samples from $x = 1.2$ (Fig. S1b). These observations suggested that a two-phase region realized for the $1.2 \leq x \leq 1.5$ compositions. The $x = 1.2$ sample contained 42.8 wt. % of $P4_2/n$ phase, the $x = 1.4$ sample – 71.2 wt. %, and the $x = 1.5$ sample – 88.9 wt. %. The $1.6 \leq x \leq 2.0$ compositions contained only the $P4_2/n$ phase. Note that we also observed traces of a pyrochlore-type phase in majority of samples, (see, for example, Fig. 1), but since it is not a perovskite-type phase, it is not discussed further; the $1.6 \leq x \leq 2.0$ samples also contained a small amount (about 1–2 wt. %, except $x = 1.7$ with about 3.6 wt. %) of a GdFeO_3 -type $Pnma$ impurity. The $x = 1.9$ and 2.0 samples additionally contained small amounts of an unknown impurity; all impurity peaks could be indexed in space group $R\bar{3}$ with $a = 7.4552 \text{ \AA}$ and $c = 8.8154 \text{ \AA}$ (for $x = 1.9$) and with $a = 7.4667 \text{ \AA}$ and $c = 8.8133 \text{ \AA}$ (for $x = 2.0$). We also note that the $x = 1$ (and $x = 1.2$) sample showed a very weak (111) reflection (the inset of Fig. 1a), which is forbidden in the $P4_2/nmc$ structure; the appearance of this reflection could originate from short-range order of Mn and Sb at the B sites.

Structure parameters of $\text{Nd}_2\text{MnMn}(\text{MnTi}_3)\text{O}_{12}$ with space group $P4_2/nmc$ and $\text{Nd}_2\text{MnMn}(\text{Mn}_2\text{Sb}_2)\text{O}_{12}$ with space group $P4_2/n$ were used as the initial models in the Rietveld analysis of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $0.8 \leq x \leq 1.0$ and $1.5 \leq x \leq 2.0$, respectively [21, 26]. In the final structural models, the Sb content was fixed according to the target compositions because the refined occupation factors were very close to the expected ones (Tables S1–S3). The square-planar Mn1 site was split from ideal (fully occupied) sites to half-occupied sites as such models noticeably reduced an atomic displacement parameter of the Mn1 site.

To check possible anti-site disorder, only Nd was assumed at the Nd site, and only Mn was assumed at Mn1 and Mn2 sites in intermediate structural models. Refined occupations factors, g , of such models are summarized on Fig. 2c. $g(\text{Nd})$ values were slightly smaller than 1. On the other hand, $2^*g(\text{Mn1})$ and $g(\text{Mn2})$ values were higher than 1. All these facts suggested the presence of anti-site disorder. Anti-site disorder monotonically decreased with increasing the x value and almost vanished in the $x = 2.0$ sample. In the final structural models, the occupations factors of the Nd, Mn1, and Mn2 sites were refined with the following constraints: $g(\text{Nd}) + g(\text{Mn}) = 1$ for the Nd and Mn2 sites and $g(\text{Nd}) + g(\text{Mn}) = 0.5$ for the split Mn1 site. The Nd content, refined in such a way, agreed quite well with the target compositions in many cases. Therefore, the total Nd content was not fixed and was refined freely.

The structural analysis of the samples with the B-site-ordered structure (space group $P4_2/n$) showed that one B site (called Mn3) was always occupied by Mn, while the second B' site (called Sb/Mn) had a mixture of Sb and Mn (Fig. 2c).

Experimental, calculated, and difference synchrotron XRPD patterns are shown in Fig. S2–S5 and Fig. 1 for the $x = 1$ sample as an example of the samples with the $P4_2/nmc$ structure and for the $x = 1.6$ sample as an example of the samples with the $P4_2/n$ structure. Refined structural parameters and bond lengths are summarized in Tables 1–2 and Tables S4–S7.

The compositional dependence of lattice parameters obtained from synchrotron XRPD data is illustrated in Fig. 3 (values are given in Table S8), where weight fractions are also given for samples containing several perovskite-type phases. Data obtained from XRPD under $\text{CuK}\alpha$ radiation for sample $0.2 \leq x \leq 1.4$ are also shown. In the samples containing (almost) the $P4_2/nmc$ phase ($0.8 \leq x \leq 1.0$), the a parameter increased monotonically, and the c parameter decreased monotonically with increasing x . On the other hand, in the samples containing (almost) the $P4_2/n$ phase ($1.6 \leq x \leq 2.0$), the a parameter increased monotonically with increasing x , and the c parameter was almost constant (see also Fig. S6).

The lattice parameters of the samples with $0.2 \leq x \leq 0.6$ continued to change monotonically and did not match with the $\text{Nd}_2\text{MnMn}(\text{Mn}_{3.2}\text{Sb}_{0.8})\text{O}_{12}$ sample ($x = 0.8$) as would be expected for $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions with the solubility limit near $x = 0.8$. These features could be explained by an additional composition variation. The $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ samples with $0.2 \leq x \leq 0.6$ had a $\text{NdMn}_7\text{O}_{12}$ impurity, which is Nd-poor in comparison with the target $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ compositions. Therefore, the main phase should be Nd-rich: $\text{Nd}_{2-y}\text{Mn}_{2-y}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$. Indeed, the refinement of the crystal structure of the $x = 0.6$ sample (from synchrotron XRPD data at RT; results are not shown) gave the following Nd-rich composition: $\text{Nd}_{2.18}\text{Mn}_{1.82}(\text{Mn}_{3.4}\text{Sb}_{0.6})\text{O}_{12}$. The $x = 0.6$ sample also showed the largest deviations of the $2^*g(\text{Mn1})$ and $g(\text{Mn2})$ occupation factors from 1 (Fig. 2c). Rare-earth-rich chemical compositions were observed before in such $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ -type perovskites, for example, in $\text{Gd}_{2.13}\text{Mn}_{5.87}\text{O}_{12}$ [27]. The formation of rare-earth-rich compositions can be explained as follows. $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ quadruple perovskites with the distinct A, A', and A'' sites are formed through the $a^*a^*c^-$ tilts with large tilt angles (large deviations of the B–O–B angles from 180°) [8]. However, the difference between the A, A', and A'' sites will be reduced when the tilt angles are reduced. Therefore, the A' and A'' sites can accommodate large Nd^{3+} cations through the local reduction in structural distortions, and such areas can be considered as tilt defects in the structure, for example, by analogy with stacking fault defects in layered materials.

We also note that the use of smaller rare-earth cations, such as Sm^{3+} [28], can significantly expand the stability range of the $P4_2/nmc$ B-site-disordered structure as $\text{Sm}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions with such a structure were formed for $0.5 \leq x \leq 1.0$ [28].

3.2. Crystal structure descriptions

The bond-valence-sum (BVS) [29] values for the Nd site (+2.84 to +3.04) were close to the expected value of +3. The BVS values for the Mn1 and Mn2 sites were close to the expected value of +2 even through small fractions of Mn^{3+} cations should present at the Mn1 site in the $x = 0.8$ and 0.9 samples. The Mn–O bond lengths for the square-planar Mn1 sites and tetrahedral Mn2 sites were nearly the same for the samples with the B-site-ordered structure with space group $P4_2/n$ and with $1.5 \leq x \leq 2.0$ (Fig. 2a). In addition, they were also close to the Mn–O bond lengths reported in the literature for the $x = 2$ sample and obtained using single-crystal data [21]. The

Mn3–O and Sb/Mn–O bond lengths in the $1.5 \leq x \leq 2.0$ samples were also close to those bond lengths reported in the literature for the $x = 2$ sample (Fig. 2b) [21]. Therefore, our structural results from synchrotron powder X-ray diffraction data are consistent with the results from single-crystal X-ray data.

The two crystal structures are shown in Fig. 4. Both two structures have two in-phase and one out-of-phase tilts of the BO_6 (or B/B'O₆) octahedra (the tilt system of $a^*b^*c^-$) and three types of A cations: 10-coordinated Nd (A), 4-coordinated square-planar Mn1 (A'), and 4-coordinated tetrahedral Mn2 (A''). The original columnar-type arrangements of A cations were observed in all samples while the occupation of the B-site was disordered (a mixture of Mn and Sb) in the $x = 0.8$ –1.0 samples, and B cations were ordered in the rock-salt-type manner in the $x = 1.6$ –2.0 samples in such a way that one B site (Mn3) is always occupied by Mn, while the second B' site (Sb/Mn) has a mixture of Sb and Mn.

The B-site-ordered structure is formed for compositions with $x > 1.5$ (for $x = 1.5$, an ideal charge distribution is $\text{Nd}_2\text{Mn}^{2+}\text{Mn}^{2+}(\text{Mn}^{2+}\text{Mn}^{3+})_B(\text{Mn}^{3+}_{0.5}\text{Sb}^{5+}_{1.5})_B\text{O}_{12}$). In other words, B-site ordering happens from the composition, where the charge difference between average oxidation states of cations at the B and B' sites exceeds 2. This is consistent with the general tendency emphasized in the literature [9].

3.3. Magnetic properties of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$

The samples with $x = 1.0$ and 1.6 were taken as representatives in each structural region and detailed magnetic properties are reported in the main text, while detailed magnetic properties of other samples are given in Fig. S7–S9. The ZFC and FCC magnetic susceptibility curves (χ versus T) measured at $H = 100$ Oe and 10 kOe are shown in Fig. 5. All samples demonstrated two obvious transitions on the ZFC and FCC χ versus T curves below T_{C1} and T_{C2} , where T_C is a ferrimagnetic Curie temperature. T_C was determined from sharp peaks on the 100 Oe FCC $d\chi/dT$ versus T curves. The T_C values of all the samples are shown in Fig. 6 and also summarized in Table 3. As shown in Fig. 5 (see also Fig. S8–S9), there were clear divergences between the 100 Oe ZFC and FCC curves just below T_{C1} , while the 10 kOe ZFC and FCC curves almost coincided with each other in the whole temperature range. Below T_{C1} , magnetic susceptibilities increased sharply indicating the appearance of a noticeable ferromagnetic component. Below T_{C2} , magnetic susceptibilities dropped at $H = 100$ Oe apparently looking as an antiferromagnetic (AFM) transition, but they showed an additional increase at $H = 10$ kOe. Magnetic structures were determined from neutron powder diffraction for the $x = 2.0$ sample [21]. It was found that a spin reorientation transition takes place and the Nd sublattice starts to order below T_{C2} . Therefore, the drop of magnetic susceptibilities below T_{C2} at $H = 100$ Oe can be explained by a spin reorientation transition, where spins are aligned perpendicular to their initial direction and to the direction of a magnetic field resulting in an apparent decrease of ordered magnetic moments along the direction of a magnetic field. However, a measurement magnetic field of $H = 10$ kOe, which is above the coercive fields (see below), can align spins along the direction of a magnetic field resulting in a continuous increase of magnetic susceptibilities below T_{C2} as total ordered moments continue to increase [21]. The positions of peaks on the FCC $d\chi/dT$ versus T curves near T_{C1} were almost independent of a magnetic field. On the other hand, the peak positions near T_{C2} noticeably depended on the measured magnetic field (100 Oe or 10 kOe, see Fig. S10 and S11). Therefore, Fig. 6b also shows the T_{C2} values at different magnetic fields. In the B-site-ordered $P4_2/n$

phases, T_{C1} monotonically decreased (from 77 K to 63 K) and T_{C2} monotonically increased (from 19 K to 39 K) for $1.6 \leq x \leq 2.0$.

The samples with $x = 1.2, 1.4$, and 1.5 , which contained both $P4_2/nmc$ and $P4_2/n$ phases, clearly showed two magnetic anomalies at higher temperatures in the region of T_{C1} (clearly seen on the 100 Oe FCC dx/dT versus T curves (the insets in Fig. S7 and S9)). The T_{C1} values associated with the $P4_2/nmc$ phase increased almost linearly from 66 K in the $x = 0.8$ sample to 97 K in the $x = 1.5$ sample. We note that the observed magnetic anomalies cannot be caused by the presence of small amounts of a pyrochlore-type impurity. Moreover, the $x = 1.4$ sample did not contain any detectable impurities (even on high quality synchrotron XRPD data). Therefore, the observed magnetic anomalies should originate from the $P4_2/nmc$ and $P4_2/n$ phases. The observed behaviour of the $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions at $1.2 \leq x \leq 1.5$ does not correspond to a classical solid solution at an equilibrium state, where properties of each phase inside a two-phase region should match with properties of phases at the solid solution boundaries. The lattice parameters of the $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions at $1.2 \leq x \leq 1.5$ continue to change with the composition especially for the $P4_2/nmc$ phase (Fig. 3). All these facts suggest a non-equilibrium state, where chemical compositions of each phase at $1.2 \leq x \leq 1.5$ continue to vary with x .

We note that there is evidence for the third magnetic transition in the $1.7 \leq x \leq 2.0$ samples with $T_{C3} = 13$ K ($x = 1.7$) and $T_{C3} = 20$ K ($x = 2.0$). It can be clearly seen from the appearance of the third additional peak on the 10 kOe differential dx/dT versus T curves (Fig. S11). The third transition was also observed in Ref. 21 in the $x = 2.0$ sample (Fig. S6c in Ref. 21); however, this transition was not noticed and discussed. No clear specific heat anomalies were detected near T_{C3} (Fig. S17). From the reported magnetic structure for the $x = 2.0$ sample [21], we can suggest that the third transition (or an additional rise of magnetic susceptibilities) could be associated with the rise of the ordered moment on the Nd sublattice. The third transition could not be caused by an unknown impurity in the $x = 1.9$ and 2.0 samples as the $x = 1.7$ and 1.8 samples did not contain this impurity.

The inverse magnetic susceptibilities followed the Curie-Weiss law at high temperatures above about 200 K, and the FCC data at $H = 10$ kOe were fit by the Curie-Weiss equation between 200 K and 395 K.

$$\chi(T) = \mu_{\text{eff}}^2 N (3k_B(T - \theta))^{-1}$$

where μ_{eff} is the effective magnetic moment, N is Avogadro's number, k_B is Boltzmann's constant, and θ is the Curie-Weiss temperature. The obtained values are summarized in Table 3, where μ_{cal} was calculated using $3.5 \mu_B$ for Nd^{3+} [30]. The observed magnetic moments (μ_{eff}) agree with the theoretically predicted spin-only moments (μ_{calc}).

Isothermal magnetization curves (M versus H) for the samples with $x = 1.0$ and 1.6 at different temperatures are illustrated in Fig. 7a and 7b, and in Fig. S12–S13 for other samples. Parameters of the M versus H curves are summarized in Table 3 and Fig. S14. The M versus H curves of all (nearly single-phase) samples at 5 K are shown in Fig. 7c; they demonstrated step-like hysteresis with small coercive fields H_C (0.36 kOe to 4.02 kOe) which is typical for ferrimagnetic materials. The extrapolated remnant magnetization ($M_R(\text{extr.})$) at $T = 5$ K was obtained by the extrapolation between 40 kOe and 70 kOe to zero field. The investigation of the magnetic structure of the $x = 2.0$ sample found that the Mn^{2+} sublattices cancel each other leaving only the Nd^{3+} uncompensated moment, and the refined ordered moment was $1.1 \mu_B$ per Nd [21]. This value is in very good agreement with the $M_R(\text{extr.})$ value ($= 2.1 \mu_B$) observed for the $x = 2.0$ sample. The $M_R(\text{extr.})$ values rapidly increased with decreasing x and reached about $5 \mu_B$ for the $x = 1.0$ sample; this is what is expected in this

sample with an ideal charge distribution of $\text{Nd}_2\text{Mn}^{2+}\text{Mn}^{2+}(\text{Mn}^{3+}_3\text{Sb}^{5+})\text{O}_{12}$, where two Nd^{3+} and approximately one Mn^{3+} (approximately, because ordered moments for Mn^{2+} and Mn^{3+} are different) could now be uncompensated.

Fig. 8 gives the results of specific heat measurements of the samples with $x = 1.0$ and 1.6 at $H = 0$ and 90 kOe, Fig. S15–S18 – for other samples. The large anomalies were observed at T_{C1} and weaker anomalies were observed at T_{C2} for all samples confirming long-range ordering. Specific heat was measured on cooling and heating for the $x = 1.6$ and 2.0 samples, but no hysteresis was detected suggesting magnetic phase transitions of the second order (Fig. S19).

4. Conclusions

In conclusion, we prepared $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $0.2 \leq x \leq 2.0$ which belong to the A-site columnar-ordered quadruple perovskite subfamily. Their crystal structures were studied by synchrotron powder X-ray diffraction at room temperature, and cation distributions were determined. Small degrees of anti-site disorder between the Nd and Mn sites were found. We found a transformation from the A-site columnar-ordered and B-site disordered structure to the A-site columnar-ordered and B-site rock-salt ordered structure. In the B-site rock-salt ordered structures, one B site was solely occupied by Mn, the second B site had a mixture of Sb and Mn. Two ferrimagnetic transitions were found with evidence for the third transition in the $1.7 \leq x \leq 2.0$ compositional range.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (No. JP22H04601) from the Japan Society for the Promotion of Science and the Kazuchika Okura Memorial Foundation (No. 2022-11). Synchrotron radiation was used at the powder diffraction beamline BL02B2 at SPring-8, with permission from the Japan Synchrotron Radiation Research Institute (Proposal Numbers: 2023A1496 and 2023B1676). We thank Dr. S. Kobayashi for his help at BL02B2 of SPring-8. MANA is supported by the World Premier International Research Center Initiative (WPI), MEXT, Japan.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2024>.

References

- [1] J.G. Bednorz, K.A. Müller, Perovskite-type oxides-The new approach to high- T_c superconductivity, *Rev. Mod. Phys.*, 60 (1988) 585–600.
- [2] K. Hirose, R. Sinmyo, J. Hernlund, Perovskite in Earth's deep interior, *Science*, 358 (2017) 734–738.

- [3] W.-J. Yin, B. Weng, J. Ge, Q. Sun, Z. Li, Y. Yan, Oxide perovskites, double perovskites and derivatives for electrocatalysis, photocatalysis, and photovoltaics, *Energ. Environ. Sci.*, 12 (2019) 442-462.
- [4] Y. Zhang, X. Feng, Z. Zheng, Z. Zhang, K. Lin, X. Sun, G. Wang, J. Wang, J. Wei, P. Vallobra, Y. He, Z. Wang, L. Chen, K. Zhang, Y. Xu, W. Zhao, Ferrimagnets for spintronic devices: From materials to applications, *Appl. Phys. Rev.*, 10 (2023) 011301.
- [5] A.M. Glazer, The classification of tilted octahedra in perovskites, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 28 (1972) 3384-3392.
- [6] A.A. Belik, R.D. Johnson, D.D. Khalyavin, The rich physics of A-site-ordered quadruple perovskite manganites $\text{AMn}_7\text{O}_{12}$, *Dalton Trans.*, 50 (2021) 15458-15472.
- [7] Y. Long, A-site ordered quadruple perovskite oxides $\text{AA}'_3\text{B}_4\text{O}_{12}$, *Chin. Phys. B*, 25 (2016) 078108.
- [8] A.A. Belik, Rise of A-site columnar-ordered $\text{A}_2\text{A}'\text{A}''\text{B}_4\text{O}_{12}$ quadruple perovskites with intrinsic triple order, *Dalton Trans.*, 47 (2018) 3209-3217.
- [9] A.M. Abakumov, A.A. Tsirlin, E.V. Antipov, Transition-Metal Perovskites, in: J. Reedijk, K. Poeppelmeier (Eds.) *Comprehensive Inorganic Chemistry II: From Elements to Applications* 2nd, Elsevier, Amsterdam, 2013, pp. 1-40.
- [10] S. Vasala, M. Karppinen, $\text{A}_2\text{B}'\text{B}''\text{O}_6$ perovskites: A review, *Prog. Solid State Chem.*, 43 (2015) 1-36.
- [11] K. Ji, K.N. Alharbi, E. Solana-Madruga, G.T. Moyo, C. Ritter, J.P. Attfield, Double Double to Double Perovskite Transformations in Quaternary Manganese Oxides, *Angew. Chem. Int. Ed.*, 60 (2021) 22248-22252.
- [12] G. King, P.M. Woodward, Cation ordering in perovskites, *J. Mater. Chem.*, 20 (2010) 5785-5796.
- [13] M.C. Knapp, P.M. Woodward, A-site cation ordering in $\text{AA}'\text{BB}'\text{O}_6$ perovskites, *J. Solid State Chem.*, 179 (2006) 1076-1085.
- [14] A.A. Belik, D.D. Khalyavin, L. Zhang, Y. Matsushita, Y. Katsuya, M. Tanaka, R.D. Johnson, K. Yamaura, Intrinsic Triple Order in A-site Columnar-Ordered Quadruple Perovskites: Proof of Concept, *ChemPhysChem*, 19 (2018) 2449-2452.
- [15] R. Liu, D.D. Khalyavin, N. Tsunoda, Y. Kumagai, F. Oba, Y. Katsuya, M. Tanaka, K. Yamaura, A.A. Belik, Spin-Glass Magnetic Properties of A-Site Columnar-Ordered Quadruple Perovskites $\text{Y}_2\text{MnGa}(\text{Mn}_{4-x}\text{Ga}_x)\text{O}_{12}$ with $0 \leq x \leq 3$, *Inorg. Chem.*, 58 (2019) 14830-14841.
- [16] A.A. Belik, D.D. Khalyavin, Y. Matsushita, K. Yamaura, Triple A-Site Cation Ordering in the Ferrimagnetic $\text{Y}_2\text{CuGaMn}_4\text{O}_{12}$ Perovskite, *Inorg. Chem.*, 61 (2022) 14428-14435.
- [17] A.A. Belik, Anisotropic Thermal Expansion and a Second-Order Charge Order Transition in the Ferrimagnetic $\text{Dy}_2\text{CuZnMn}_4\text{O}_{12}$ Perovskite with Triple A-Site Cation Ordering, *Inorg. Chem.*, 62 (2023) 20042-20049.
- [18] F. Millange, V. Caignaert, B. Domengès, B. Raveau, E. Suard, Order-Disorder Phenomena in New $\text{LaBaMn}_2\text{O}_{6-x}$ CMR Perovskites. Crystal and Magnetic Structure, *Chem. Mater.*, 10 (1998) 1974-1983.
- [19] Z. Deng, C.J. Kang, M. Croft, W. Li, X. Shen, J. Zhao, R. Yu, C. Jin, G. Kotliar, S. Liu, T.A. Tyson, R. Tapper, M. Greenblatt, A Pressure-Induced Inverse Order-Disorder Transition in Double Perovskites, *Angew. Chem. Int. Ed.*, 59 (2020) 8240-8246.
- [20] R. Scatena, R. Liu, V.V. Shvartsman, D.D. Khalyavin, Y. Inaguma, K. Yamaura, A.A. Belik, R.D. Johnson, Hybrid Improper Ferroelectricity in Columnar $(\text{NaY})\text{MnMnTi}_4\text{O}_{12}$, *Angew. Chem. Int. Ed.*, 62 (2023) e202305994.
- [21] E. Solana-Madruga, A.M. Arevalo-Lopez, A.J. Dos Santos-Garcia, E. Urones-Garrote, D. Avila-Brandé, R. Saez-Puche, J.P. Attfield, Double Double Cation Order in the High-Pressure Perovskites MnRMnSbO_6 , *Angew. Chem. Int. Ed.*, 55 (2016) 9340-9344.
- [22] S. Kawaguchi, M. Takemoto, K. Osaka, E. Nishibori, C. Moriyoshi, Y. Kubota, Y. Kuroiwa, K. Sugimoto, High-throughput powder diffraction measurement system consisting of multiple MYTHEN detectors at beamline BL02B2 of SPring-8, *Rev. Sci. Instrum.*, 88 (2017) 085111.
- [23] F. Izumi, T. Ikeda, A Rietveld-Analysis Programm RIETAN-98 and its Applications to Zeolites, *Mater. Sci. Forum*, 321-324 (2000) 198-205.
- [24] G. Shimura, K. Niwa, Y. Shirako, M. Hasegawa, High-Pressure Synthesis and Magnetic Behavior of A-Site Columnar-Ordered Double Perovskites, $\text{LnMn}(\text{Ga}_{0.5}\text{Ti}_{0.5})_2\text{O}_6$ (Ln = Sm, Gd), *Eur. J. Inorg. Chem.*, 2017 (2017) 835-839.
- [25] K. Leinenweber, J. Parise, High-pressure synthesis and crystal structure of $\text{CaFeTi}_2\text{O}_6$, a new perovskite structure type, *J. Solid State Chem.*, 114 (1995) 277-281.
- [26] R. Liu, M. Tanaka, H. Mori, Y. Inaguma, K. Yamaura, A.A. Belik, Ferrimagnetic and Relaxor Ferroelectric Properties of $\text{R}_2\text{MnMn}(\text{MnTi}_3)\text{O}_{12}$ Perovskites with R = Nd, Eu, and Gd, *J. Mater. Chem. C*, 9 (2021) 947-956.
- [27] A.A. Belik, L. Zhang, Y. Matsushita, Y. Katsuya, M. Tanaka, K. Yamaura, Crystal structures of cation non-stoichiometric RMn_3O_6 (R = Gd, Er, and Tm) manganites belonging to A-site columnar-ordered quadruple perovskite family, *J. Solid State Chem.*, 275 (2019) 43-48.
- [28] X. Liang, K. Yamaura, A.A. Belik, Three perovskite phases with different cation orders in $\text{Sm}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$, *Chem. Eur. J.*, 30 (2024) e202401960.
- [29] N.E. Brese, M. O'Keeffe, Bond-valence parameters for solids, *Acta Crystallogr., Sect. B: Struct. Sci.*, 47 (1991) 192-197.
- [30] C. Kittel, *Introduction to Solid State Physics*, John Wiley & Sons, Inc: New York, New York, 2005.

Table 1 Structure parameters of Nd₂MnMn(Mn_{4-x}Sb_x)O₁₂ ($x = 0.8, 0.9$, and 1.0) at $T = 295$ K from synchrotron X-ray powder diffraction data

x	0.8	0.9	1
a (Å)	7.58349(2)	7.59899(2)	7.62652(2)
c (Å)	7.92523(2)	7.91997(3)	7.89916(3)
V (Å ³)	455.775(2)	457.336(2)	459.445(3)
$g(\text{Nd})$	0.890(3)Nd+0.110Mn	0.892(4)Nd+0.108Mn	0.880(3)Nd+0.120Mn
$z(\text{Nd})$	0.22303(7)	0.22296(8)	0.22309(7)
$B(\text{Nd})$ (Å ²)	1.291(11)	1.233(13)	1.241(12)
$g(\text{Mn1-SQ})$	0.424(3)Mn+0.076Nd	0.447(2)Mn+0.053Nd	0.423(3)Mn+0.077Nd
$z(\text{Mn1})$	0.7867(4)	0.7854(4)	0.7871(4)
$B(\text{Mn1})$ (Å ²)	1.65(8)	1.00	2.05(10)
$g(\text{Mn2-T})$	0.884(5)Mn+0.116Nd	0.888(4)Mn+0.112Nd	0.900(5)Mn+0.100Nd
$B(\text{Mn2})$ (Å ²)	1.00(6)	1.00	0.93(6)
$g(\text{Mn/Sb-Oc})$	0.8Mn+0.2Sb	0.775Mn+0.225Sb	0.75Mn+0.25Sb
$B(\text{Mn/Sb})$ (Å ²)	0.932(15)	0.969(16)	0.939(16)
$y(\text{O1})$	0.0572(5)	0.0565(6)	0.0561(5)
$z(\text{O1})$	-0.0380(6)	-0.0374(6)	-0.0356(6)
$B(\text{O1})$ (Å ²)	1.25(9)	1.06(10)	1.27(9)
$y(\text{O2})$	0.5388(6)	0.5377(6)	0.5374(6)
$z(\text{O2})$	0.5777(5)	0.5785(6)	0.5773(5)
$B(\text{O2})$ (Å ²)	1.50(10)	1.49(12)	1.18(10)
$x(\text{O3})$	0.4380(4)	0.4375(5)	0.4387(4)
$B(\text{O3})$ (Å ²)	2.24(11)	2.55(14)	2.74(12)
R_{wp} (%)	7.64	8.74	7.59
R_{p} (%)	5.46	6.22	5.46
R_{I} (%)	6.12	5.68	5.54
R_{F} (%)	8.13	7.39	7.41
Impurities	pyrochlore: 0.1% NdMn ₇ O ₁₂ : 2.3%	pyrochlore: 0.4% —	pyrochlore: 0.2% —

Crystal data: space group $P4_2/nmc$ (No. 137, cell choice 2), $Z = 2$.

Nd – $4d$ site (0.25, 0.25, z); Mn1-SQ – $4c$ site (0.75, 0.25, z) near $2a$ site (0.75, 0.25, 0.75); Mn2-T – $2b$ site (0.75, 0.25, 0.25); Mn/Sb-Oc – $8e$ site (0, 0, 0); O1 and O2 – $8g$ site (0.25, y , z), and O3 – $8f$ site (x , $-x$, 0.25).

$g(\text{O1}) = g(\text{O2}) = g(\text{O3}) = 1$, g is the occupation factor.

SQ: square-planar (site), T: tetrahedral (site), Oc: octahedral (site).

Table 2 Structure parameters of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 1.5, 1.6, \text{ and } 1.7$) at $T = 295$ K from synchrotron X-ray powder diffraction data

x	1.5	1.6	1.7
a (Å)	7.74834(2)	7.76781(4)	7.78827(2)
c (Å)	7.90920(2)	7.90366(4)	7.90647(3)
V (Å ³)	474.843(2)	476.898(4)	479.584(3)
$g(\text{Nd})$	0.902(3)Nd+0.098Mn	0.930(4)Nd+0.070Mn	0.920(4)Nd+0.080Mn
$z(\text{Nd})$	0.77703(6)	0.77703(7)	0.77691(7)
$B(\text{Nd})$ (Å ²)	0.993(11)	0.908(15)	0.825(12)
$g(\text{Mn1-SQ})$	0.463(3)Mn+0.037Nd	0.443(4)Mn+0.057Nd	0.464(3)Mn+0.036Nd
$z(\text{Mn1})$	0.7833(5)	0.7870(5)	0.7824(5)
$B(\text{Mn1})$ (Å ²)	1.70(10)	1.62(11)	1.34(10)
$g(\text{Mn2-T})$	0.970(5)Mn+0.030Nd	0.955(6)Mn+0.045Nd	0.973(5)Mn+0.027Nd
$B(\text{Mn2})$ (Å ²)	0.57(6)	0.42(7)	0.44(6)
$g(\text{Mn3-Oc})$	1Mn	1Mn	1Mn
$B(\text{Mn3})$ (Å ²)	0.86(3)	0.81(3)	0.78(3)
$g(\text{Sb/Mn-Oc})$	0.75Sb+0.25Mn	0.8Sb+0.2Mn	0.85Sb+0.15Mn
$B(\text{Sb/Mn})$ (Å ²)	0.579(13)	0.436(16)	0.408(12)
$x(\text{O1})$	−0.0433(8)	−0.0494(14)	−0.0491(11)
$y(\text{O1})$	0.5769(8)	0.5695(13)	0.5711(10)
$z(\text{O1})$	0.2365(6)	0.2339(8)	0.2338(7)
$B(\text{O1})$ (Å ²)	1.17(12)	1.51(15)	1.07(12)
$x(\text{O2})$	−0.2373(13)	−0.2373(16)	−0.2373(13)
$y(\text{O2})$	−0.0391(6)	−0.0396(7)	−0.0402(6)
$z(\text{O2})$	0.5846(5)	0.5851(7)	0.5839(6)
$B(\text{O2})$ (Å ²)	1.27(11)	1.40(14)	1.25(12)
$x(\text{O3})$	−0.2579(12)	−0.2571(15)	−0.2602(12)
$y(\text{O3})$	0.0642(5)	0.0682(6)	0.0674(6)
$z(\text{O3})$	−0.0352(5)	−0.0358(6)	−0.0343(6)
$B(\text{O3})$ (Å ²)	1.24(9)	1.06(11)	0.87(10)
R_{wp} (%)	6.44	7.70	6.96
R_{p} (%)	4.68	5.51	5.09
R_{I} (%)	3.77	2.96	2.91
R_{F} (%)	3.90	2.07	2.46
Impurities	pyrochlore: 2.0% $P4_2/nmc$ -per.: 9.1%	pyrochlore: 1.1% $Pnma$ -per.: 1.5%	pyrochlore: 1.9% $Pnma$ -per.: 3.6%

Crystal data: space group $P4_2/n$ (No. 86, cell choice 2), $Z = 2$.

Nd – 4e site (0.25, 0.75, z); Mn1-SQ – 4f site (0.25, 0.25, z); Mn2-T – 2a site (0.75, 0.75, 0.75); Mn3-Oc – 4c site (0, 0.5, 0.5); Sb/Mn-Oc – 4d site (0, 0, 0.5); O1, O2 and O3 – 8g site (x, y, z).

$g(\text{O1}) = g(\text{O2}) = g(\text{O3}) = 1$, g is the occupation factor.

SQ: square-planar (site), T: tetrahedral (site), Oc: octahedral (site).

$P4_2/nmc$ -per.: a $\text{Nd}_2\text{MnMn}(\text{Mn}_3\text{Sb})\text{O}_{12}$ -type perovskite phase with $P4_2/nmc$ symmetry.

$Pnma$ -per.: a GdFeO_3 -type perovskite phase with $Pnma$ symmetry.

Table 3 Temperatures of magnetic anomalies (T_{C1} and T_{C2}), parameters of Curie-Weiss fits, and parameters of M versus H curves at $T = 5$ K for $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $0.8 \leq x \leq 1.0$ and $1.5 \leq x \leq 2.0$.

x	T_{C1} (K)	T_{C2} (K)	$\mu_{\text{eff}} (\mu_{\text{B}}/\text{f.u.})$	$\mu_{\text{calc}} (\mu_{\text{B}}/\text{f.u.})$	θ (K)	$M_{\text{S}} (\mu_{\text{B}}/\text{f.u.})$	$M_{\text{R}} (\mu_{\text{B}}/\text{f.u.})$	$M_{\text{R}}(\text{extr.}) (\mu_{\text{B}}/\text{f.u.})$	H_{C} (kOe)
0.8	66	7	12.71(2)	12.919	-62.6(14)	5.929	3.060	4.666	0.80
0.9	70	6	12.23(2)	12.911	-61.9(12)	6.329	2.466	5.229	0.39
1.0	75	6	12.86(3)	12.903	-63.7(14)	5.921	1.574	4.996	0.36
1.5	78	17	13.376(14)	12.865	-66.0(8)	5.212	2.279	4.375	0.62
1.6	77	19	12.803(10)	12.857	-67.7(6)	4.543	2.506	3.693	0.89
1.7	74	24	12.949(11)	12.849	-76.9(7)	4.195	2.371	3.169	1.49
1.8	73	28	12.831(9)	12.841	-87.2(6)	3.655	2.315	2.913	1.95
1.9	69	32	12.697(7)	12.834	-85.0(4)	3.553	2.263	2.642	4.02
2.0	63	39	12.750(6)	12.826	-99.4(4)	3.194	1.757	2.118	1.90

Curie-Weiss fits were performed between 200 and 395 K using the FCC χ^{-1} versus T data at 10 kOe.

M_{S} is the magnetization value at $T = 5$ K and $H = 70$ kOe.

M_{R} is the remnant magnetization at $T = 5$ K.

$M_{\text{R}}(\text{extr.})$ at $T = 5$ K is obtained by the extrapolation between 40 kOe and 70 kOe to zero field.

H_{C} is the coercive field at $T = 5$ K.

T_{C} is determined from sharp peaks on the 100 Oe FCC $d\chi/dT$ versus T curves.

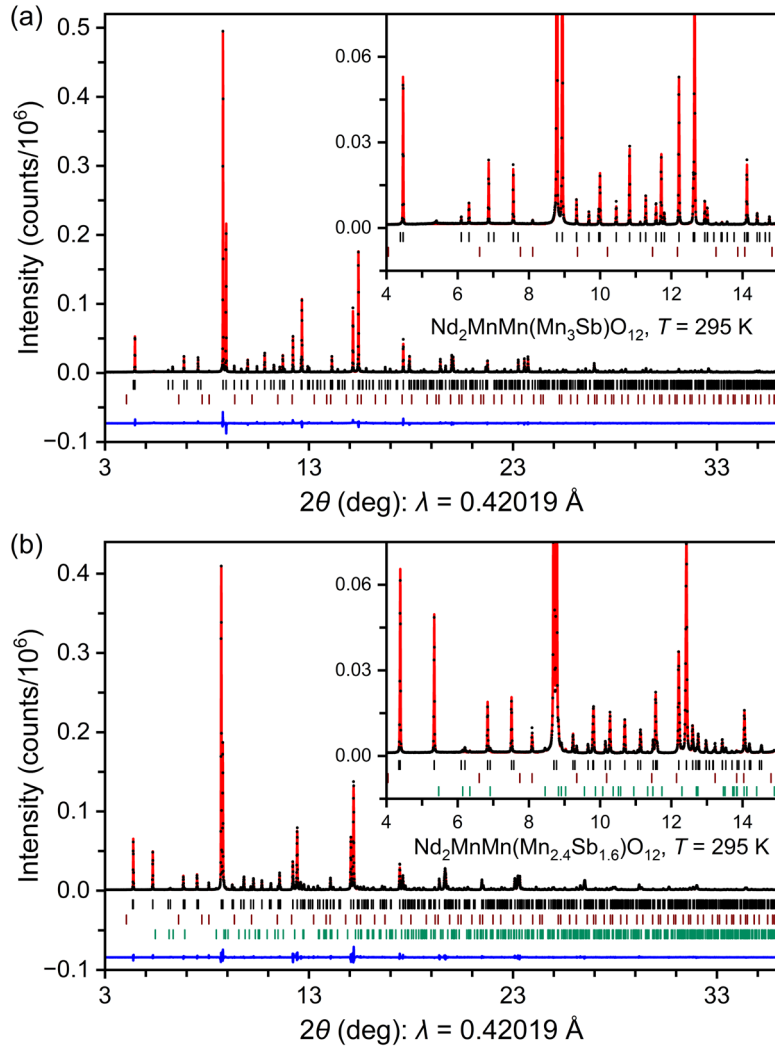


Fig. 1 Fragments of experimental (black circles), calculated (red line), and difference (blue line at the bottom) synchrotron XRPD patterns of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with (a) $x = 1.0$ and (b) $x = 1.6$ at $T = 295 \text{ K}$. The tick marks show possible Bragg reflection positions of the main perovskite phase (the first black row), pyrochlore impurity (the second brown row), and impurity with $Pnma$ symmetry (the third green row). Each inset shows a zoomed fragment.

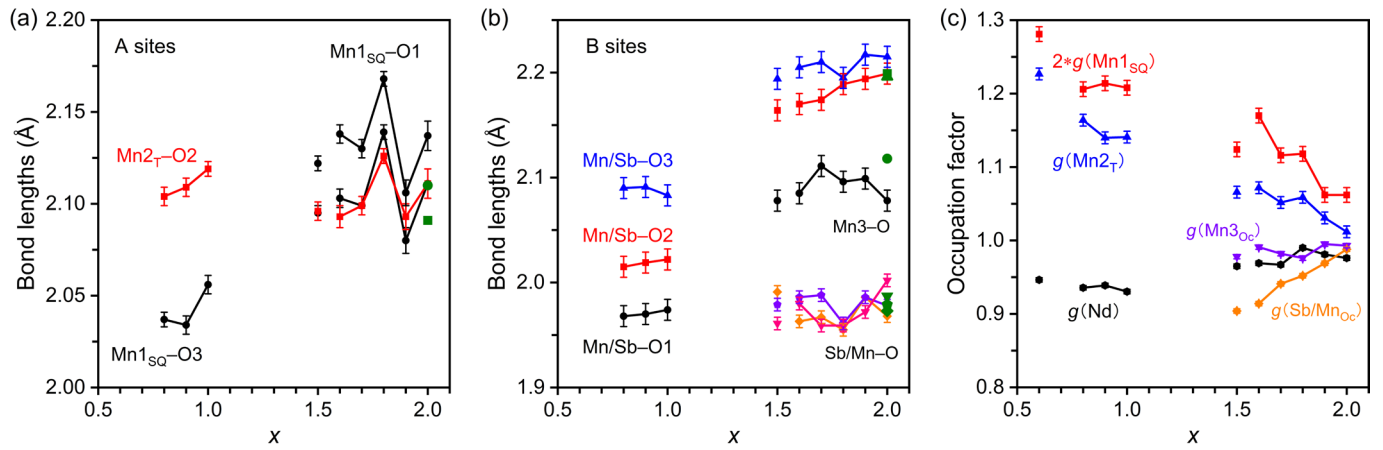


Fig. 2 Compositional dependence of (a) Mn1–O (square-planar, SQ) and Mn2–O (tetrahedral, T) bond lengths, (b) Mn/Sb–O, Mn3–O, and Sb/Mn–O (octahedral, Oc) bond lengths, and (c) cation occupation factors in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions for $x = 0.6, 0.8 \leq x \leq 1.0$, and $1.5 \leq x \leq 2.0$ from synchrotron XRPD data at $T = 295$ K. Only Mn was assumed at the Mn1, Mn2, and Mn3 sites, only Nd was assumed at the Nd site, and only Sb was assumed at the Sb/Mn site. The data presented in green symbols on panels (a) and (b) for $x = 2.0$ are sourced from the literature (the single-crystal data at $T = 120$ K) [21].

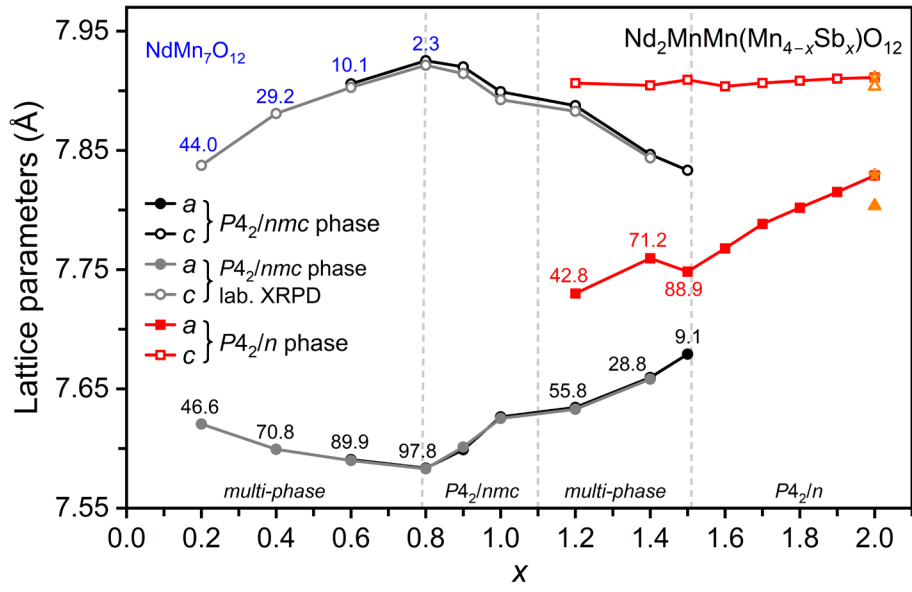


Fig. 3 Compositional dependence of the lattice parameters in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions for $0.2 \leq x \leq 2.0$ from laboratory and synchrotron XRPD data at $T = 295$ K. Numbers show weight fractions (in %) of corresponding phases for multi-phased samples; see the text and Tables 1–2 and S1–S8 for details. The data presented in orange symbols for $x = 2.0$ are sourced from the literature (triangles are based on synchrotron XRPD data at $T = 295$ K, stars are based on neutron data at $T = 200$ K [21]).

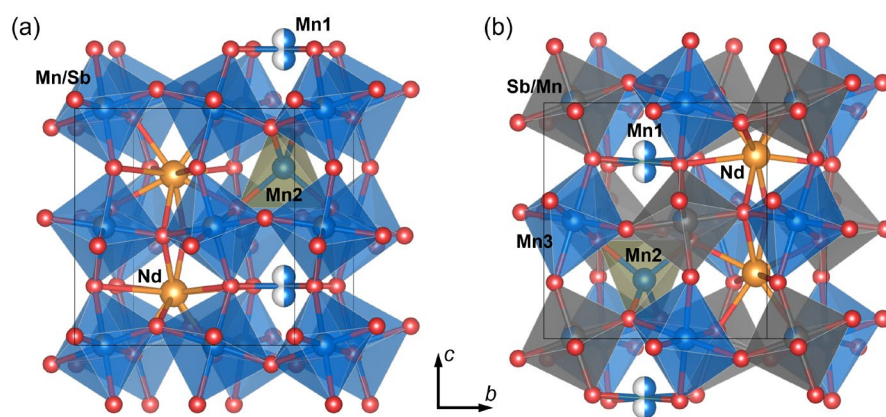


Fig. 2 Fragments of crystal structures of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with different space groups in a polyhedral presentation. (a) $P4_2/nmc$ and (b) $P4_2/n$. Mn1O_4 square-planar units, Mn2O_4 tetrahedra, $(\text{Mn/Sb})\text{O}_6$ or $(\text{Sb/Mn})\text{O}_6$ octahedra, and Mn3O_6 octahedra are shown. Nd atoms are presented by large orange spheres.

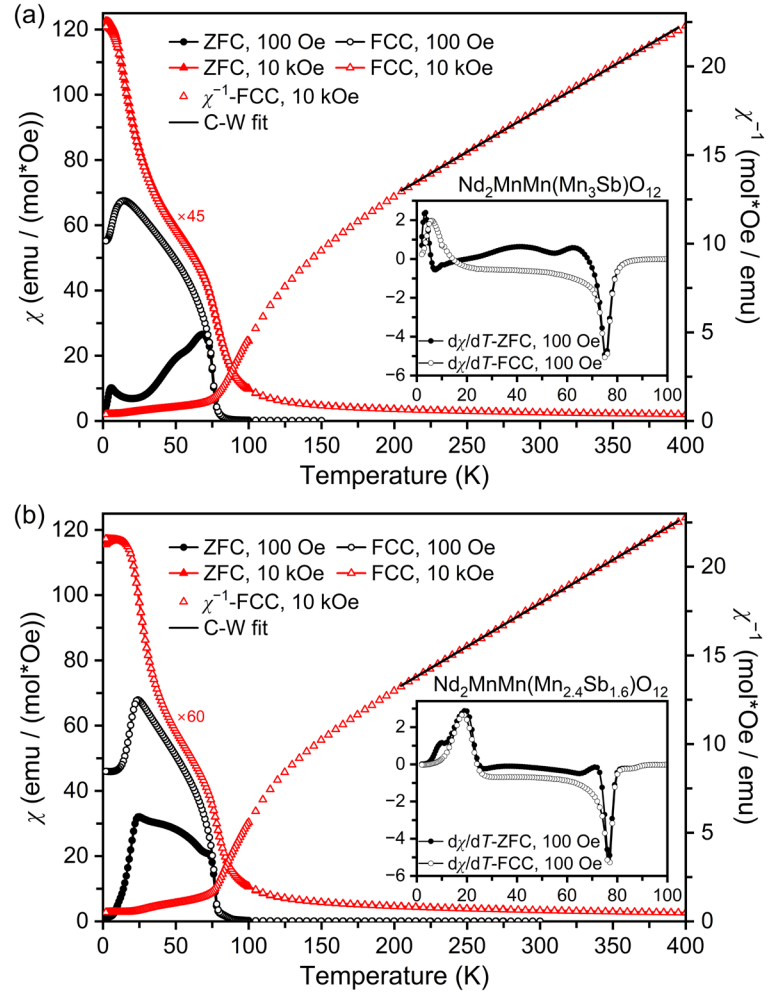


Fig. 5 ZFC (filled symbols) and FCC (empty symbols) dc magnetic susceptibility ($\chi = M/H$) curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with (a) $x = 1.0$ and (b) $x = 1.6$ measured at 100 Oe (black, circles) and 10 kOe (red, triangles). The black line gives the Curie-Weiss fit (C-W fit) based on the FCC χ^{-1} versus T curve at 10 kOe. Each inset shows 100 Oe ZFC and FCC $d\chi/dT$ versus T curves in each panel.

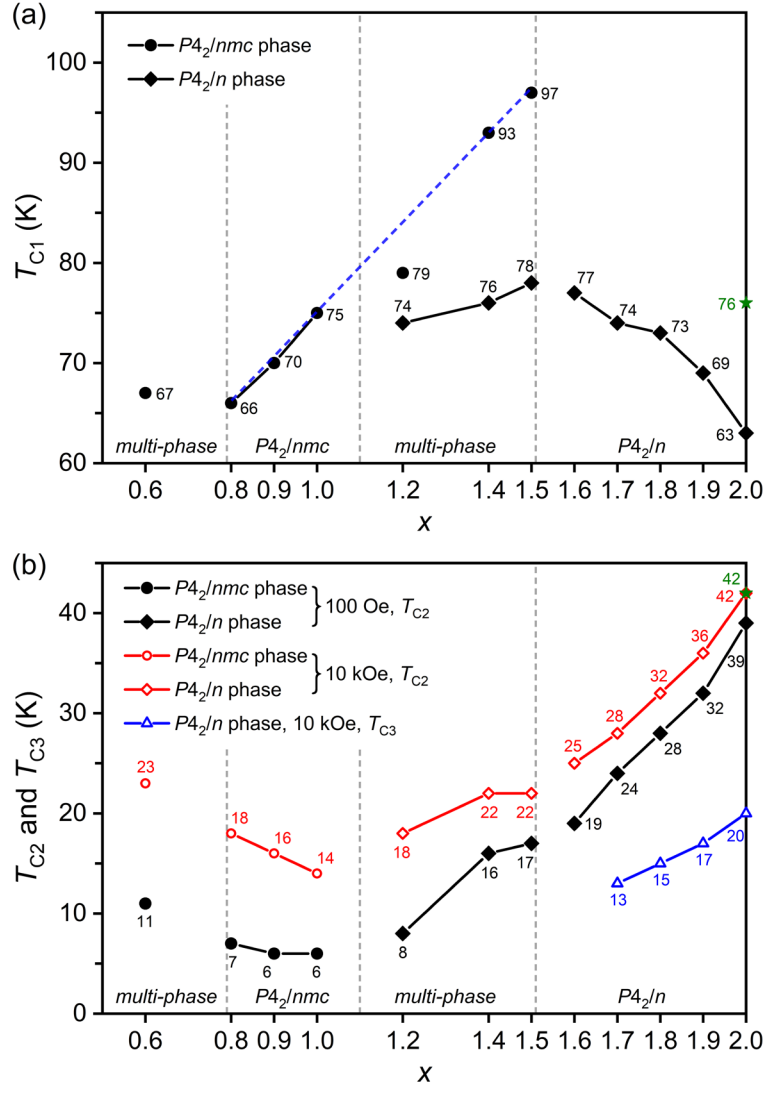


Fig. 6 The ferrimagnetic Curie temperature (T_C) of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $0.4 \leq x \leq 2.0$. (a) T_{C1} and (b) T_{C2} and T_{C3} . On panel (b): the black, filled circles show T_{C2} related to $P4_2/nmc$ phase at 100 Oe, the black, filled diamonds show T_{C2} related to $P4_2/n$ phase at 100 Oe. The red, empty circles show T_{C2} related to $P4_2/nmc$ phase at 10 kOe, the red, empty diamonds show T_C related to $P4_2/n$ phase at 10 kOe. The blue, empty triangles show T_{C3} . Numbers show the T_C values in K. The data presented in green stars are sourced from the literature [21].

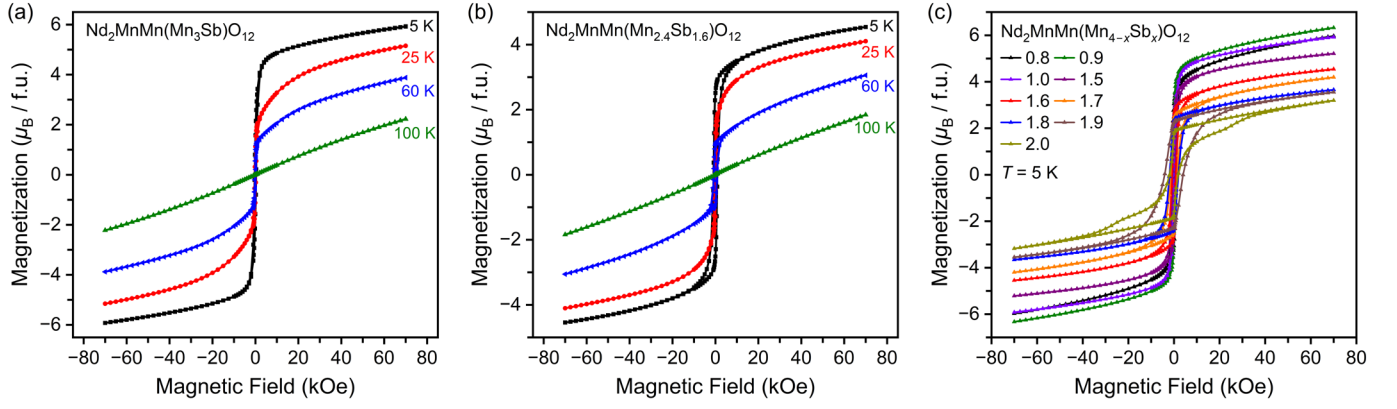


Fig. 7 M versus H curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with (a) $x = 1.0$ and (b) $x = 1.6$ at different temperatures. (c) M versus H curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $0.8 \leq x \leq 1.0$ and $1.5 \leq x \leq 2.0$ at $T = 5$ K.

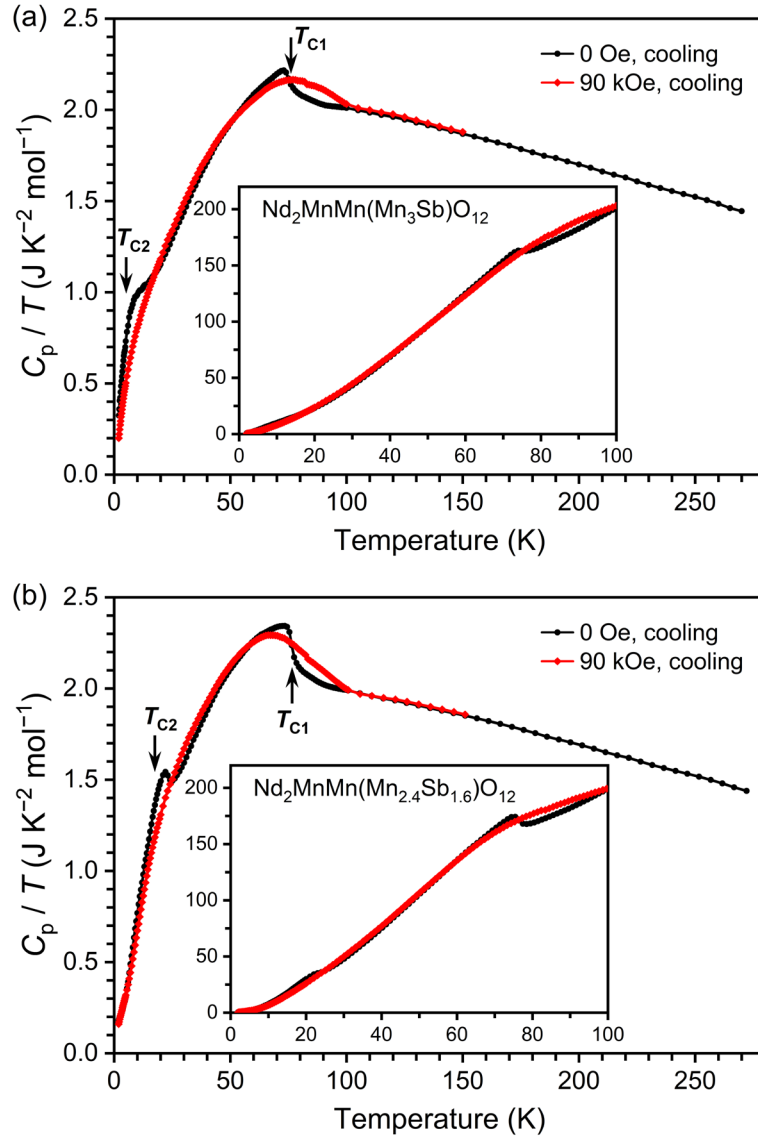


Fig. 8 Specific heat data of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with (a) $x = 1.0$ and (b) $x = 1.6$, plotted as C_p/T versus T . Measurements were performed on cooling at $H = 0$ Oe and 90 kOe. Insets present the C_p (in $\text{J K}^{-1} \text{mol}^{-1}$) versus T curves.

Supporting Information

B-site ordered and disordered phases in A-site columnar-ordered quadruple perovskites $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$

Xuan Liang ^{a,b}, Kazunari Yamaura ^{a,b}, Alexei A. Belik ^{a,*}

^a *Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

^b *Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan*

* Corresponding author.

E-mail address: Alexei.Belik@nims.go.jp (A.A. Belik)

Table S1. Results of refinements of occupation factors of the cation sites in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 0.6, 0.8, 0.9$, and 1.0); space group $P4_2/nmc$; SQ: square-planar, T: tetrahedral, Oc: octahedral.

x	0.6	0.8	0.9	1.0
$g(\text{Nd})^a$	0.946(3)	0.9356(18)	0.9388(20)	0.9304(18)
$B(\text{Nd}) (\text{\AA}^2)$	1.39(2)	1.320(11)	1.270(13)	1.275(12)
$g(\text{Mn1-SQ})$	0.641(9)	0.603(4)	0.607(5)	0.604(4)
$B(\text{Mn1}) (\text{\AA}^2)$	1.63(16)	1.41(8)	1.78(10)	1.78(9)
$g(\text{Mn2-T})$	1.227(14)	1.164(7)	1.140(7)	1.141(7)
$B(\text{Mn2}) (\text{\AA}^2)$	0.70(11)	0.87(5)	0.71(6)	0.81(6)
$g(\text{Mn/Sb-Oc})^a$	0.85Mn+0.15Sb	0.8Mn+0.2Sb	0.775Mn+0.225Sb	0.75Mn+0.25Sb
$B(\text{Mn/Sb}) (\text{\AA}^2)$	0.93(3)	0.939(15)	0.917(17)	0.943(16)
$g(\text{Mn/Sb-Oc})^b$		0.803(2)Mn+0.197Sb	0.778(3)Mn+0.222Sb	0.753(3)Mn+0.247Sb
$B(\text{Mn/Sb}) (\text{\AA}^2)$		0.922(16)	0.956(16)	0.929(16)
Impurities:				
NdMn ₇ O ₁₂	10 %, $a = 7.5861 \text{ \AA}$, $b = 7.3019 \text{ \AA}$, $c = 7.5441 \text{ \AA}$, $\beta = 91.222^\circ$	2.3 %, $a = 7.6254 \text{ \AA}$, $b = 7.2819 \text{ \AA}$, $c = 7.5637 \text{ \AA}$, $\beta = 91.210^\circ$	—	—
pyrochlore	—	0.1 %, $a = 10.2864 \text{ \AA}$	0.4 %, $a = 10.2965 \text{ \AA}$	0.2 %, $a = 10.2976 \text{ \AA}$

^a All structural and non-structural parameters were refined simultaneously except the occupation factors, $g(\text{Mn/Sb-Oc})$, of the Mn/Sb-Oc site, which were fixed at the nominal values. In this model, only Nd was assumed at the Nd site, and only Mn – at the Mn1-SQ and Mn2-T sites. Deviations from 1 (or from 0.5 for the Mn1-SQ site) indicate the presence of small anti-site disorders.

^b All structural and non-structural parameters were refined simultaneously except the $g(\text{Nd})$ for the Nd site and $g(\text{Mn1-SQ})$ for the Mn1 site, and the refinements in this model started from the results reported in Table 1 in the main text. The following constraint was used, $g(\text{Sb}) = 1 - g(\text{Mn})$, for the Mn/Sb-Oc site. These results demonstrate that the refined occupations of the Mn/Sb-Oc site were close to the nominal values.

Table S2. Results of refinements of occupation factors of the cation sites in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 1.5, 1.6, \text{ and } 1.7$); space group $P4_2/n$; SQ: square-planar, T: tetrahedral, Oc: octahedral

x	1.5	1.6	1.7
$g(\text{Nd})^a$	0.965(3)	0.969(4)	0.967(4)
$B(\text{Nd}) (\text{\AA}^2)$	1.019(11)	0.929(14)	0.848(11)
$g(\text{Mn1-SQ})$	0.562(5)	0.585(5)	0.558(5)
$B(\text{Mn1}) (\text{\AA}^2)$	1.53(9)	1.44(10)	1.21(9)
$g(\text{Mn2-T})$	1.066(8)	1.072(9)	1.052(9)
$B(\text{Mn2}) (\text{\AA}^2)$	0.55(5)	0.37(6)	0.43(6)
$g(\text{Mn3-Oc})^a$	1 fixed	1 fixed	1 fixed
$B(\text{Mn3}) (\text{\AA}^2)$	0.70(3)	0.74(4)	0.70(3)
$g(\text{Sb-Oc})$	0.904(3)	0.914(4)	0.941(3)
$B(\text{Sb}) (\text{\AA}^2)$	0.673(16)	0.489(17)	0.446(13)
$g(\text{Mn3-Oc})^b$	0.978(3)	0.991(4)	0.982(4)
$B(\text{Mn3}) (\text{\AA}^2)$	0.71(3)	0.74(4)	0.69(3)
$g(\text{Sb-Oc})$	0.760(4)Sb+0.240Mn	0.805(5)Sb+0.195Mn	0.851(4)Sb+0.149Mn
$B(\text{Sb}) (\text{\AA}^2)$	0.628(16)	0.456(17)	0.424(14)
Impurities:			
$Pnma$ -	—	1.5 %, $a = 5.7002 \text{ \AA}$,	3.6 %, $a = 5.7308 \text{ \AA}$,
GdFeO ₃ -type		$b = 7.5970 \text{ \AA}$,	$b = 7.5836 \text{ \AA}$,
		$c = 5.4087 \text{ \AA}$	$c = 5.4096 \text{ \AA}$
Pyrochlore	2.0 %, $a = 10.3148 \text{ \AA}$	1.1 %, $a = 10.3191 \text{ \AA}$	1.9 %, $a = 10.3241 \text{ \AA}$
$P4_2/nmc$	9.1 %, $a = 7.6791 \text{ \AA}$,	—	—
	$c = 7.8334 \text{ \AA}$		

^a All structural and non-structural parameters were refined simultaneously except for the occupation factors, $g(\text{Mn3-Oc})$, of the Mn3-Oc site, which were fixed at unity. In this model, only Nd was assumed at the Nd site, only Mn – at the Mn1-SQ, Mn2-T, and Mn3-Oc sites, and only Sb – at the Sb-Oc site. Deviations from 1 (or from 0.5 for the Mn1-SQ site) indicate the presence of small anti-site disorders.

^b All structural and non-structural parameters were refined simultaneously except for the $g(\text{Nd})$ for the Nd site and $g(\text{Mn1-SQ})$ for the Mn1 site, and the refinements in this model started from the results reported in Table 2 in the main text. The following constraint was used, $g(\text{Mn}) = 1 - g(\text{Sb})$, for the Sb-Oc site. These results demonstrate that the refined occupations of the Sb-Oc site were close to the nominal values.

Table S3. Results of refinements of occupation factors of the cation sites in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 1.8, 1.9, \text{ and } 2.0$); space group $P4_2/n$; SQ: square-planar, T: tetrahedral, Oc: octahedral

x	1.8	1.9	2.0
$g(\text{Nd})^a$	0.990(4)	0.981(6)	0.976(7)
$B(\text{Nd}) (\text{\AA}^2)$	0.806(10)	0.704(13)	0.620(14)
$g(\text{Mn1-SQ})$	0.559(5)	0.531(8)	0.531(9)
$B(\text{Mn1}) (\text{\AA}^2)$	0.96(8)	0.96(12)	0.79(12)
$g(\text{Mn2-T})$	1.059(8)	1.031(13)	1.012(15)
$B(\text{Mn2}) (\text{\AA}^2)$	0.52(5)	0.42(7)	0.35(8)
$g(\text{Mn3-Oc})^a$	1 fixed	1 fixed	1 fixed
$B(\text{Mn3}) (\text{\AA}^2)$	0.72(3)	0.65(4)	0.63(4)
$g(\text{Sb-Oc})$	0.952(3)	0.969(5)	0.988(6)
$B(\text{Sb}) (\text{\AA}^2)$	0.398(11)	0.401(16)	0.365(17)
$g(\text{Mn3-Oc})^b$	0.976(3)	0.995(6)	0.993(6)
$B(\text{Mn3}) (\text{\AA}^2)$	0.63(3)	0.61(4)	0.58(4)
$g(\text{Sb-Oc})$	0.891(4)Sb+0.109Mn	0.944(7)Sb+0.056Mn	0.984(8)Sb+0.016Mn
$B(\text{Sb}) (\text{\AA}^2)$	0.383(11)	0.393(17)	0.360(17)
Impurities:			
<i>Pnma</i> -	1.0 %, $a = 5.7503 \text{ \AA}$,	0.5 %, $a = 5.7764 \text{ \AA}$,	0.5 %, $a = 5.8020 \text{ \AA}$,
GdFeO ₃ -type	$b = 7.5842 \text{ \AA}$,	$b = 7.5775 \text{ \AA}$,	$b = 7.5721 \text{ \AA}$,
	$c = 5.4106 \text{ \AA}$	$c = 5.4152 \text{ \AA}$	$c = 5.4184 \text{ \AA}$
pyrochlore	1.5 %, $a = 10.3349 \text{ \AA}$	0.3 %, $a = 10.3381 \text{ \AA}$	—
unknown	—	$a = b = 7.4552 \text{ \AA}$,	$a = b = 7.4667 \text{ \AA}$,
phase ^c		$c = 8.8154 \text{ \AA}$,	$c = 8.8133 \text{ \AA}$,
		$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

^a All structural and non-structural parameters were refined simultaneously except for the occupation factors, $g(\text{Mn3-Oc})$, of the Mn3-Oc site, which were fixed at unity. In this model, only Nd was assumed at the Nd site, only Mn – at the Mn1-SQ, Mn2-T, and Mn3-Oc sites, and only Sb – at the Sb-Oc site. Deviations from 1 (or from 0.5 for the Mn1-SQ site) indicate the presence of small anti-site disorders.

^b All structural and non-structural parameters were refined simultaneously except for the $g(\text{Nd})$ for the Nd site and $g(\text{Mn1-SQ})$ for the Mn1 site, and the refinements in this model started from the results reported in Table S4. The following constraint was used, $g(\text{Mn}) =$

$1 - g(\text{Sb})$, for the Sb-Oc site. These results demonstrate that the refined occupations of the Sb-Oc site were close to the nominal values.

^c All reflections of an unknown phase could be indexed in space group $R\bar{3}$.

Table S4. Structure parameters of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 1.8, 1.9$, and 2.0) at $T = 295$ K from synchrotron X-ray powder diffraction data

x	1.8	1.9	2
a (Å)	7.80190(2)	7.81513(3)	7.82890(3)
c (Å)	7.90843(2)	7.91024(3)	7.91111(4)
V (Å ³)	481.394(2)	483.128(3)	484.886(4)
$g(\text{Nd})$	0.982(4)Nd+0.018Mn	0.978(6)Nd+0.022Mn	0.974(7)Nd+0.026Mn
$z(\text{Nd})$	0.77672(2)	0.77681(9)	0.77667(10)
$B(\text{Nd})$ (Å ²)	0.800(10)	0.700(14)	0.614(14)
$g(\text{Mn1-SQ})$	0.457(3)Mn+0.043Nd	0.474(5)Mn+0.026Nd	0.469(5)Mn+0.031Nd
$z(\text{Mn1})$	0.7806(5)	0.7783(8)	0.7772(8)
$B(\text{Mn1})$ (Å ²)	1.11(8)	1.05(13)	0.92(13)
$g(\text{Mn2-T})$	0.960(5)Mn+0.040Nd	0.974(8)Mn+0.026Nd	1Mn
$B(\text{Mn2})$ (Å ²)	0.55(5)	0.45(8)	0.29(7)
$g(\text{Mn3-Oc})$	1Mn	1Mn	1Mn
$B(\text{Mn3})$ (Å ²)	0.73(2)	0.63(3)	0.58(3)
$g(\text{Sb/Mn-Oc})$	0.9Sb+0.1Mn	0.95Sb+0.05Mn	1Sb
$B(\text{Sb/Mn})$ (Å ²)	0.381(10)	0.398(16)	0.379(16)
$x(\text{O1})$	−0.0489(11)	−0.0485(14)	−0.0473(15)
$y(\text{O1})$	0.5641(11)	0.5768(13)	0.5726(15)
$z(\text{O1})$	0.2341(6)	0.2355(10)	0.2335(11)
$B(\text{O1})$ (Å ²)	0.79(11)	0.80(17)	0.67(18)
$x(\text{O2})$	−0.2345(11)	−0.2358(17)	−0.2349(20)
$y(\text{O2})$	−0.0389(6)	−0.0419(9)	−0.0404(10)
$z(\text{O2})$	0.5808(6)	0.5839(9)	0.5827(10)
$B(\text{O2})$ (Å ²)	0.59(10)	0.89(16)	0.71(17)
$x(\text{O3})$	−0.2591(10)	−0.2585(16)	−0.2551(17)
$y(\text{O3})$	0.0628(5)	0.0659(8)	0.0663(9)
$z(\text{O3})$	−0.0326(5)	−0.0312(9)	−0.0313(9)
$B(\text{O3})$ (Å ²)	0.57(8)	0.59(12)	0.52(13)
R_{wp} (%)	7.38	12.01	13.12
R_{p} (%)	5.22	6.64	6.91
R_{I} (%)	3.26	4.42	4.71
R_{F} (%)	3.06	3.24	3.08
Impurities	pyrochlore: 1.5% <i>Pnma</i> -per.: 1.0%	pyrochlore: 0.3% <i>Pnma</i> -per.: 0.5%	— <i>Pnma</i> -per.: 0.5%

Crystal data: space group $P4_2/n$ (No. 86, cell choice 2), $Z = 2$.

Nd – $4e$ site (0.25, 0.75, z); Mn1-SQ – $4f$ site (0.25, 0.25, z); Mn2-T – $2a$ site (0.75, 0.75, 0.75); Mn3-Oc – $4c$ site (0, 0.5, 0.5); Sb/Mn-Oc – $4d$ site (0, 0, 0.5); O1, O2 and O3 – $8g$ site (x , y , z).

$g(O1) = g(O2) = g(O3) = 1$, g is the occupation factor.

SQ: square-planar (site), T: tetrahedral (site), Oc: octahedral (site).

Pnma-per.: a $GdFeO_3$ -type perovskite phase with *Pnma* symmetry.

Because of the presence of an unidentified impurity in the $x = 1.9$ and 2.0 samples, only a ratio of the weight fractions of the phases is relevant (not absolute values).

Table S5. Bond lengths, bond angles, bond-valence sum (BVS), and distortion parameters of (Mn/Sb)O₆ (Δ) in Nd₂MnMn(Mn_{4-x}Sb_x)O₁₂ ($x = 0.8, 0.9$, and 1.0) at $T = 295$ K from synchrotron X-ray powder diffraction data

x	0.8	0.9	1.0
Nd–O1 (Å) $\times 2$	2.393(4)	2.401(5)	2.413(4)
Nd–O1 (Å) $\times 2$	2.533(4)	2.533(5)	2.476(4)
Nd–O2 (Å) $\times 2$	2.475(4)	2.467(5)	2.522(4)
Nd–O3 (Å) $\times 4$	2.771(1)	2.778(1)	2.785(11)
BVS(Nd ³⁺)	+3.04	+3.03	+2.99
Mn1–O3 (Å) $\times 4$	2.037(4)	2.034(5)	2.056(5)
Mn1–O2 (Å) $\times 2$	2.808(4)	2.827(5)	2.808(5)
Mn1–O1 (Å) $\times 2$	3.065(5)	3.067(5)	3.050(5)
Mn1–Mn1	0.581(6)	0.561(7)	0.586(7)
BVS(Mn1 ²⁺)	+2.24	+2.25	+2.14
Mn2–O2 (Å) $\times 4$	2.104(5)	2.109(5)	2.119(4)
Mn2–O1 (Å) $\times 4$	2.872(4)	2.874(4)	2.884(4)
BVS(Mn2 ²⁺)	+1.93	+1.90	+1.85
Mn/Sb–O1 (Å) $\times 2$	1.968(1)	1.970(1)	1.974(1)
Mn/Sb–O2 (Å) $\times 2$	2.015(2)	2.019(2)	2.022(1)
Mn/Sb–O3 (Å) $\times 2$	2.090(1)	2.091(2)	2.083(1)
$\Delta(\text{Mn/Sb})$	6.2×10^{-4}	6.0×10^{-4}	4.8×10^{-4}
BVS(Mn ³⁺)	+2.96	+2.94	+2.94
BVS(Sb ⁵⁺)	+4.85	+4.81	+4.81
Mn/Sb–O1–Mn/Sb $\times 2$	148.9(3)	149.3(3)	149.9(3)
Mn/Sb–O2–Mn/Sb $\times 2$	140.4(3)	140.4(3)	141.1(3)
Mn/Sb–O3–Mn/Sb $\times 2$	142.89(12)	142.50(13)	142.96(12)

BVS = $\sum_{i=1}^N v_i$, $v_i = \exp[(R_0 - l_i)/B]$, N is the coordination number, $B = 0.37$, $R_0(\text{Nd}^{3+}) = 2.117$, $R_0(\text{Mn}^{2+}) = 1.79$, $R_0(\text{Mn}^{3+}) = 1.76$, $R_0(\text{Sb}^{5+}) = 1.942$.

Table S6. Bond lengths, bond angles, bond-valence sum (BVS), and distortion parameters of Mn_3O_6 and $(\text{Sb}/\text{Mn})\text{O}_6$ (Δ) in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 1.5, 1.6, \text{ and } 1.7$) at $T = 295$ K from synchrotron X-ray powder diffraction data

x	1.5	1.6	1.7
Nd–O1 (Å) $\times 2$	2.659(8)	2.737(14)	2.951(11)
Nd–O1 (Å) $\times 2$	2.998(8)	2.932(14)	2.736(11)
Nd–O2 (Å) $\times 2$	2.495(4)	2.502(5)	2.516(5)
Nd–O3 (Å) $\times 2$	2.395(4)	2.373(5)	2.389(4)
Nd–O3 (Å) $\times 2$	2.499(4)	2.486(5)	2.484(4)
BVS(Nd^{3+})	+3.02	+3.04	+2.97
Mn1–O3 (Å) $\times 2$	3.147(5)	3.159(6)	3.176(6)
Mn1–O2 (Å) $\times 2$	2.891(5)	2.869(6)	2.892(6)
Mn1–O1 (Å) $\times 2$	2.095(4)	2.103(5)	2.099(5)
Mn1–O1 (Å) $\times 2$	2.122(4)	2.138(5)	2.130(5)
Mn1–Mn1	0.526(7)	0.585(8)	0.512(8)
BVS(Mn^{2+})	+1.85	+1.80	+1.81
Mn2–O3 (Å) $\times 4$	2.969(4)	2.996(5)	3.005(4)
Mn2–O2 (Å) $\times 4$	2.096(5)	2.093(6)	2.099(5)
BVS(Mn^{2+})	+1.91	+1.92	+1.89
Mn3–O1 (Å) $\times 2$	2.194(5)	2.205(6)	2.210(5)
Mn3–O2 (Å) $\times 2$	2.164(10)	2.170(12)	2.174(10)
Mn3–O3 (Å) $\times 2$	2.078(9)	2.085(11)	2.111(10)
$\Delta(\text{Mn3})$	5.2×10^{-4}	5.5×10^{-4}	3.5×10^{-4}
BVS(Mn^{3+})	+2.32	+2.27	+2.19
Sb/Mn–O1 (Å) $\times 2$	1.991(5)	1.963(6)	1.967(5)
Sb/Mn–O2 (Å) $\times 2$	1.979(10)	1.986(12)	1.988(10)
Sb/Mn–O3 (Å) $\times 2$	1.961(9)	1.980(11)	1.959(9)
$\Delta(\text{Sb}/\text{Mn})$	4.0×10^{-5}	2.4×10^{-5}	3.9×10^{-5}
BVS(Sb^{5+})	+5.46	+5.47	+5.54
BVS(Mn^{3+})	+3.34	+3.34	+3.39
Mn3–O1–Sb/Mn $\times 2$	141.8(4)	142.8(6)	142.3(5)
Mn3–O2–Sb/Mn $\times 2$	138.4(3)	138.2(3)	138.6(3)
Mn3–O3–Sb/Mn $\times 2$	147.2(3)	145.6(3)	146.2(3)

$\text{BVS} = \sum_{i=1}^N v_i$, $v_i = \exp[(R_0 - l_i)/B]$, N is the coordination number, $B = 0.37$, $R_0(\text{Nd}^{3+}) = 2.117$, $R_0(\text{Mn}^{2+}) = 1.79$, $R_0(\text{Mn}^{3+}) = 1.76$, $R_0(\text{Sb}^{5+}) = 1.942$.

Table S7. Bond lengths, bond angles, bond-valence sum (BVS), and distortion parameters of Mn_3O_6 and $(\text{Sb}/\text{Mn})\text{O}_6$ (Δ) in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ ($x = 1.8, 1.9$, and 2.0) at $T = 295$ K from synchrotron X-ray powder diffraction data

x	1.8	1.9	2.0
Nd–O1 ($\text{\AA}$) $\times 2$	2.767(11)	2.718(13)	2.732(15)
Nd–O1 ($\text{\AA}$) $\times 2$	2.911(11)	3.002(13)	2.984(15)
Nd–O2 ($\text{\AA}$) $\times 2$	2.523(4)	2.536(7)	2.534(8)
Nd–O3 ($\text{\AA}$) $\times 2$	2.422(4)	2.419(7)	2.416(7)
Nd–O3 ($\text{\AA}$) $\times 2$	2.497(4)	2.475(7)	2.476(7)
BVS(Nd^{3+})	+2.84	+2.87	+2.87
Mn1–O3 ($\text{\AA}$) $\times 2$	3.151(5)	3.178(8)	3.190(1)
Mn1–O2 ($\text{\AA}$) $\times 2$	2.892(5)	2.196(9)	2.924(8)
Mn1–O1 ($\text{\AA}$) $\times 2$	2.139(4)	2.080(7)	2.111(8)
Mn1–O1 ($\text{\AA}$) $\times 2$	2.168(4)	2.106(7)	2.137(8)
Mn1–Mn1	0.485(7)	0.448(13)	0.430(13)
BVS(Mn^{2+})	+1.65	+1.91	+1.76
Mn2–O3 ($\text{\AA}$) $\times 4$	2.986(5)	3.016(7)	3.021(7)
Mn2–O2 ($\text{\AA}$) $\times 4$	2.126(4)	2.093(7)	2.111(8)
BVS(Mn^{2+})	+1.77	+1.91	+1.82
Mn3–O1 ($\text{\AA}$) $\times 2$	2.195(5)	2.217(8)	2.215(8)
Mn3–O2 ($\text{\AA}$) $\times 2$	2.189(8)	2.194(13)	2.199(14)
Mn3–O3 ($\text{\AA}$) $\times 2$	2.096(8)	2.099(12)	2.078(13)
$\Delta(\text{Mn3})$	4.4×10^{-4}	5.5×10^{-4}	8.0×10^{-4}
BVS(Mn^{3+})	+2.22	+2.17	+2.22
Sb/Mn–O1 ($\text{\AA}$) $\times 2$	1.955(5)	1.986(8)	1.968(9)
Sb/Mn–O2 ($\text{\AA}$) $\times 2$	1.961(8)	1.986(13)	1.978(14)
Sb/Mn–O3 ($\text{\AA}$) $\times 2$	1.959(8)	1.972(12)	2.002(13)
$\Delta(\text{Sb}/\text{Mn})$	1.7×10^{-6}	1.1×10^{-5}	5.2×10^{-5}
BVS(Sb^{5+})	+5.74	+5.40	+5.38
BVS(Mn^{3+})	+3.51	+3.30	–
Mn3–O1–Sb/Mn $\times 2$	144.6(5)	140.4(6)	142.0(7)
Mn3–O2–Sb/Mn $\times 2$	140.0(3)	138.4(4)	147.6(3)
Mn3–O3–Sb/Mn $\times 2$	148.3(3)	147.4(4)	147.3(4)

$\text{BVS} = \sum_{i=1}^N v_i$, $v_i = \exp[(R_0 - l_i)/B]$, N is the coordination number, $B = 0.37$, $R_0(\text{Nd}^{3+}) = 2.117$, $R_0(\text{Mn}^{2+}) = 1.79$, $R_0(\text{Mn}^{3+}) = 1.76$, $R_0(\text{Sb}^{5+}) = 1.942$.

Table S8. Lattice parameters and symmetry of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ at $T = 295$ K from X-ray powder diffraction ($\text{CuK}\alpha$ radiation) data and synchrotron X-ray powder diffraction data

x	Symmetry	a (Å)	c (Å)	data source
0.2	$P4_2/nmc$	7.62054	7.83736	
0.4	$P4_2/nmc$	7.59926	7.88087	X-ray
0.6	$P4_2/nmc$	7.58994	7.90285	powder
0.8	$P4_2/nmc$	7.58303	7.92141	diffraction
0.9	$P4_2/nmc$	7.6012	7.9144	(lab.
1.0	$P4_2/nmc$	7.6252	7.8925	$\text{CuK}\alpha$
1.2	$P4_2/nmc$	7.6329	7.8828	radiation)
	$P4_2/n$	7.7349	7.9024	data
1.4	$P4_2/nmc$	7.6582	7.8437	
	$P4_2/n$	7.7577	7.9034	
0.6	$P4_2/nmc$	7.59071	7.90578	
0.8	$P4_2/nmc$	7.58349	7.92523	
0.9	$P4_2/nmc$	7.59899	7.91997	
1.0	$P4_2/nmc$	7.62652	7.89916	
1.2	$P4_2/nmc$	7.63438	7.88749	
	$P4_2/n$	7.73002	7.90639	synchrotron
1.4	$P4_2/nmc$	7.65951	7.84658	X-ray
	$P4_2/n$	7.75955	7.90452	powder
1.5	$P4_2/n$	7.74834	7.90920	diffraction
	$P4_2/nmc$	7.67908	7.83334	data
1.6	$P4_2/n$	7.76781	7.90366	
1.7	$P4_2/n$	7.78827	7.90647	
1.8	$P4_2/n$	7.80190	7.90843	
1.9	$P4_2/n$	7.81513	7.91024	
2.0	$P4_2/n$	7.82890	7.91111	

For tetragonal symmetries ($P4_2/nmc$ and $P4_2/n$), $a = b$ and $\alpha = \beta = \gamma = 90^\circ$.

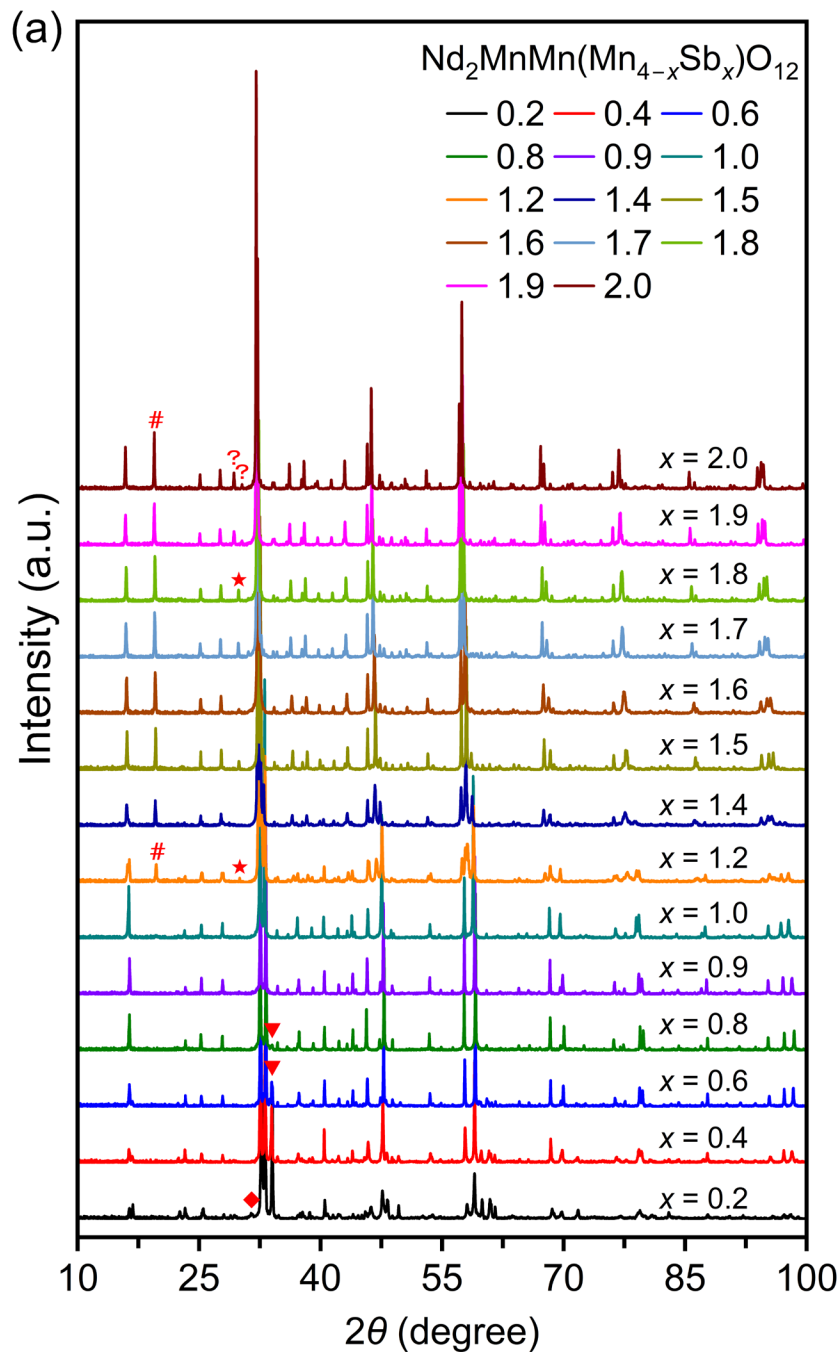


Fig. S1a. X-ray powder diffraction patterns of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 0.2, 0.4, 0.6, 0.8, 0.9, 1.0, 1.2, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9$, and 2.0 at $T = 295$ K (CuK α radiation). The red octothorpes show the characteristic peak of the $P4_2/n$ phase (with the Miller index of (111)). The red stars show the 100% peak of a pyrochlore-type phase. The red triangles show a characteristic peak of $\text{NdMn}_7\text{O}_{12}$. The red square shows a characteristic peak of NdMnO_3 . The red question marks show unknown impurity.

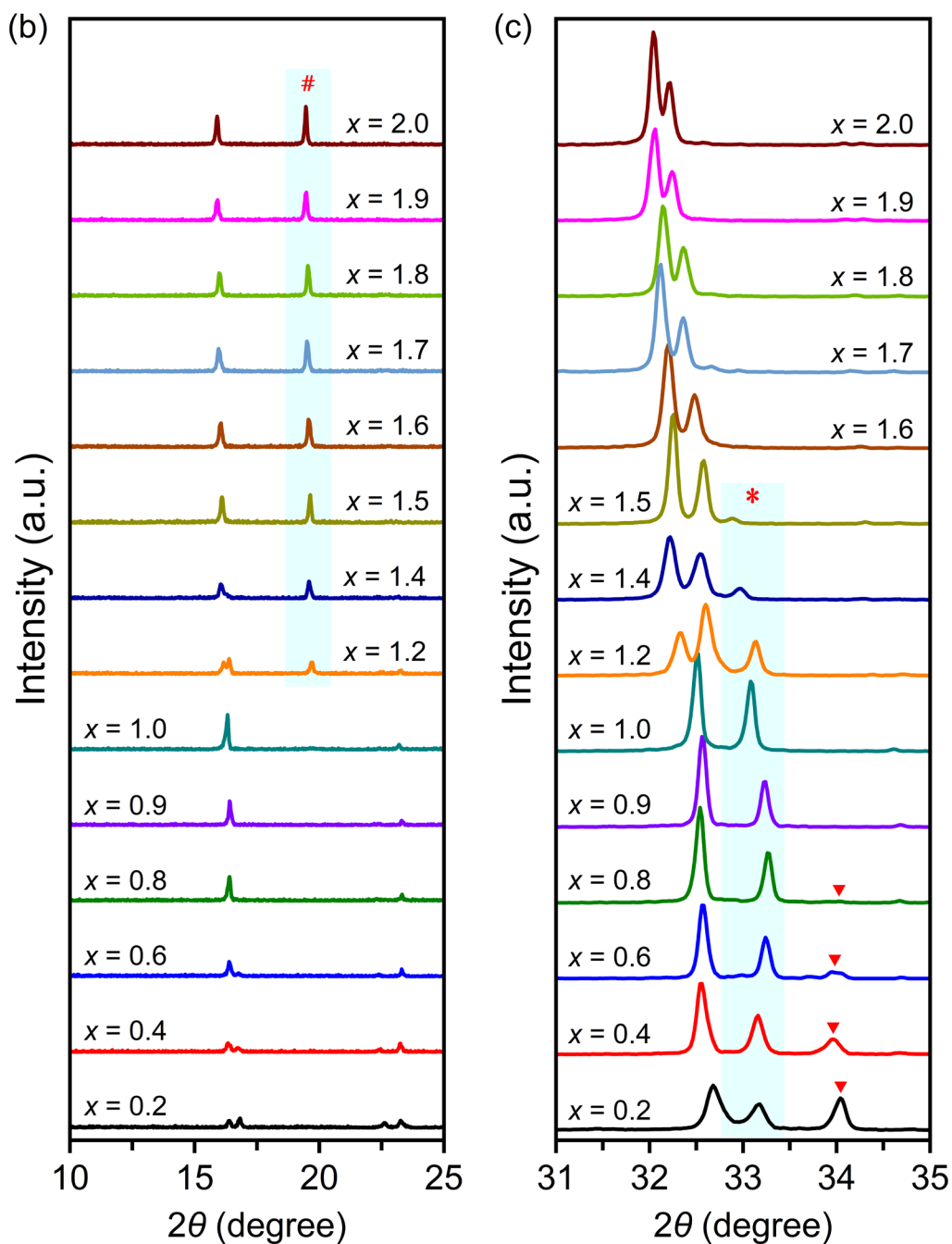


Fig. S1b and S1c. Fragments of X-ray powder diffraction patterns of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with different x values at $T = 295\text{ K}$ ($\text{CuK}\alpha$ radiation). The red octahedron shows characteristic peak of the $P4_2/n$ phase (with the Miller index of (111)). The red asterisk shows a characteristic peak of the $P4_2/nmc$ phase. The red triangles show a characteristic peak of $\text{NdMn}_7\text{O}_{12}$.

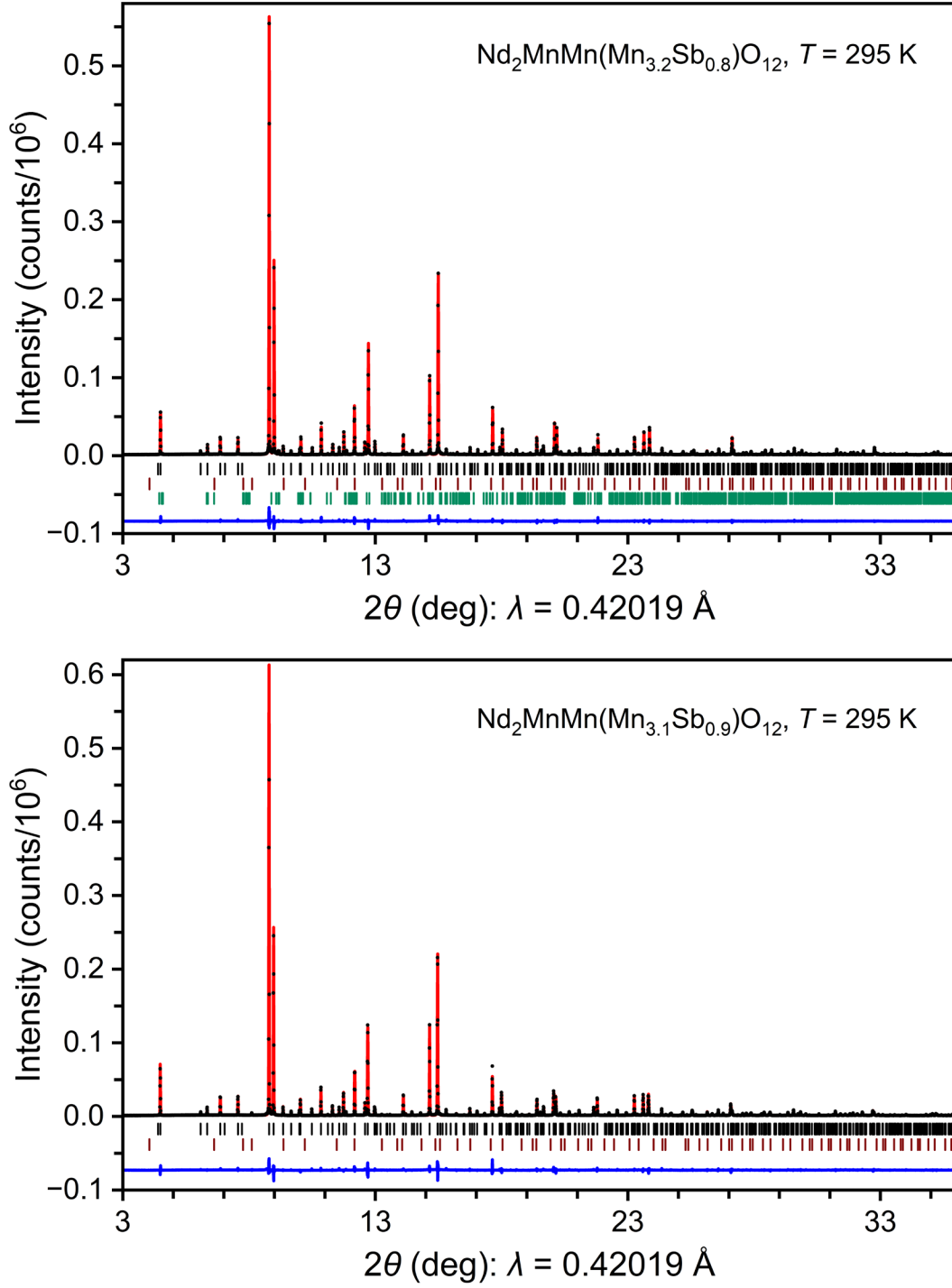


Fig. S2. Fragments of experimental (black circles), calculated (red line), and difference (blue line) synchrotron XRPD patterns of Nd₂MnMn(Mn_{4-x}Sb_x)O₁₂ with $x = 0.8$ and 0.9 at $T = 295$ K. The tick marks show possible Bragg reflection positions of the main perovskite phase ($P4_2/nmc$ phase, the first row), pyrochlore impurity (the second row), and NdMn₇O₁₂ impurity (the third row, only appears in the sample with $x = 0.8$).

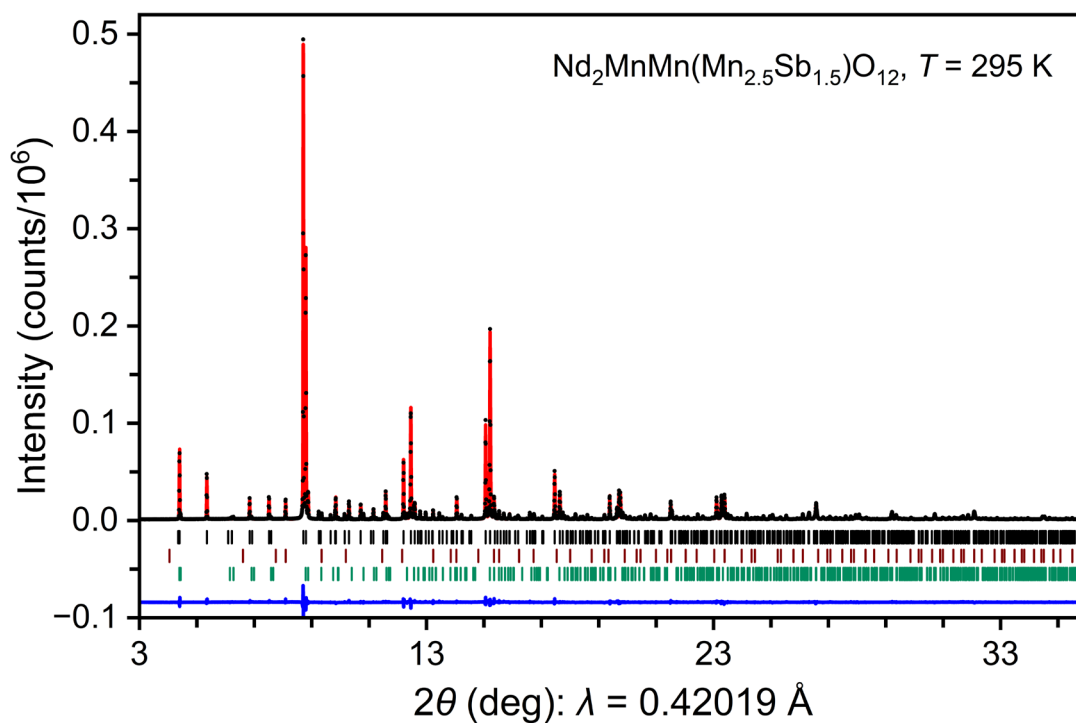


Fig. S3. Fragments of experimental (black circles), calculated (red line), and difference (blue line) synchrotron XRPD patterns of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.5$ at $T = 295$ K. The tick marks show possible Bragg reflection positions of the main perovskite phase ($P4_2/n$ phase, the first row), pyrochlore impurity (the second row), and $P4_2/nmc$ phase (the third row).

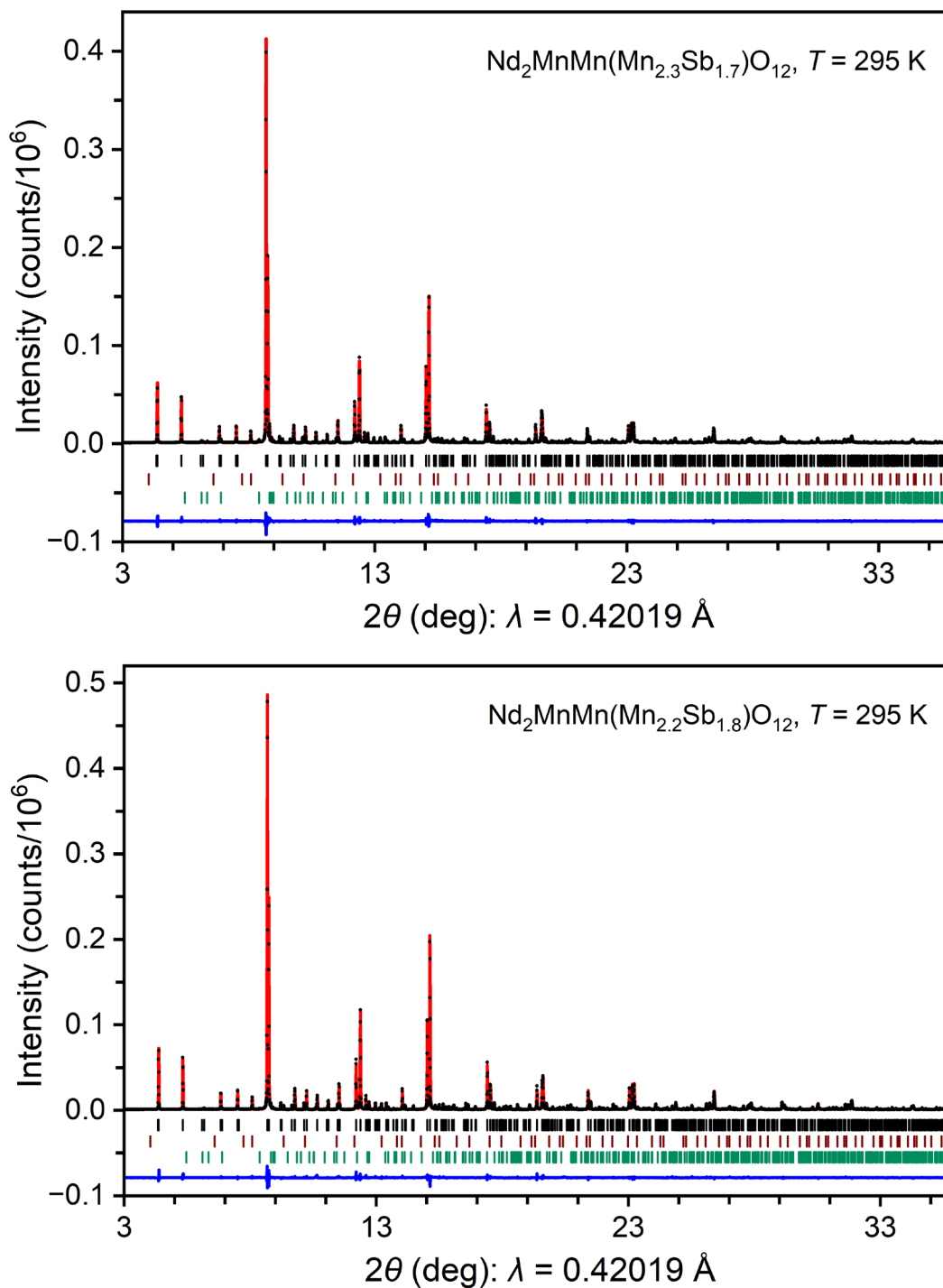


Fig. S4. Fragments of experimental (black circles), calculated (red line), and difference (blue line) synchrotron XRPD patterns of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.7$ and 1.8 at $T = 295$ K. The tick marks show possible Bragg reflection positions of the main perovskite phase (*P*4₂/*n* phase, the first row), pyrochlore impurity (the second row), and impurity with *Pnma* symmetry (the third row).

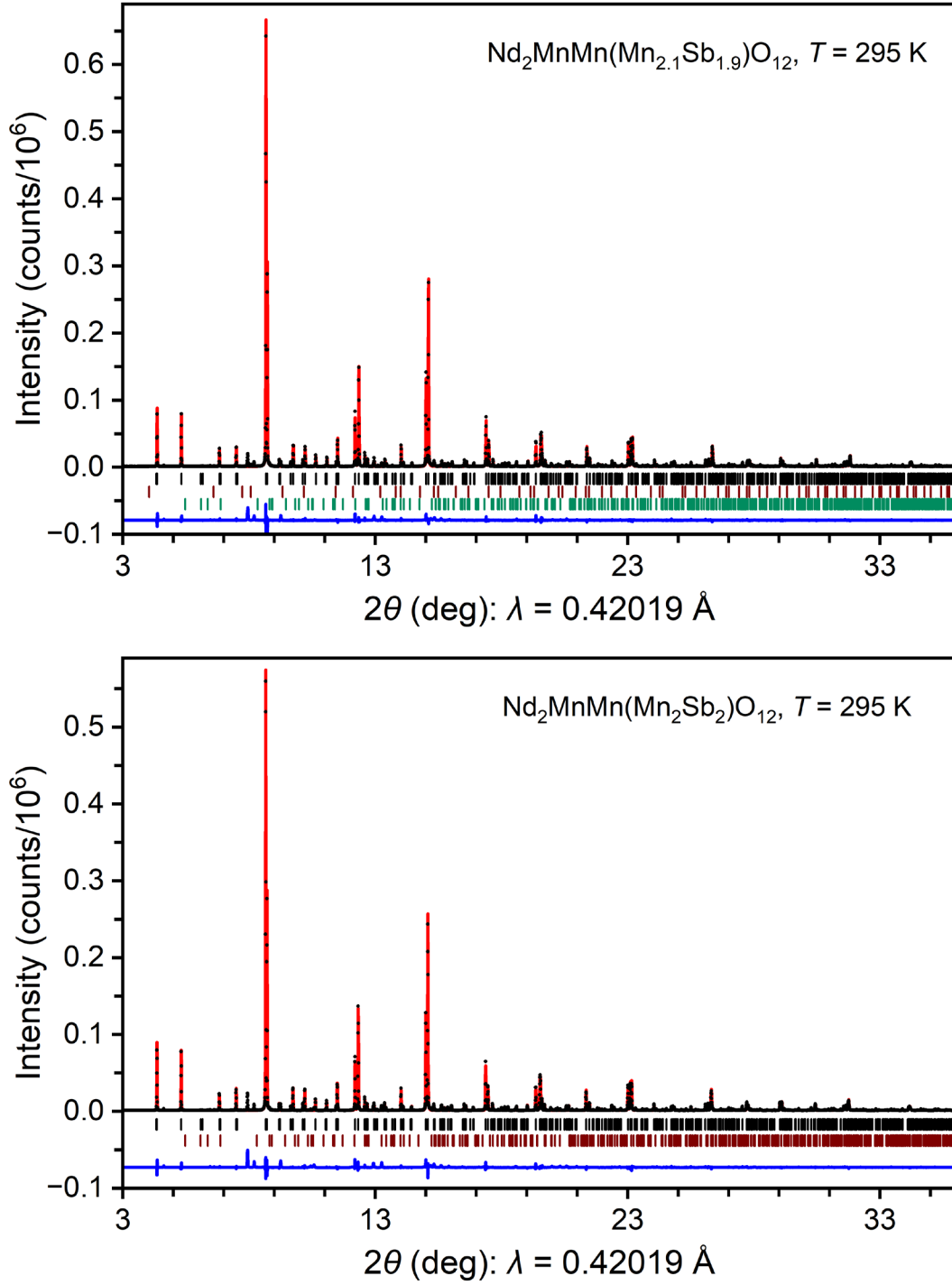


Fig. S5. Fragments of experimental (black circles), calculated (red line), and difference (blue line) synchrotron XRPD patterns of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.9$ and 2.0 at $T = 295 \text{ K}$. For samples with $x = 1.9$, the tick marks show possible Bragg reflection positions of the main perovskite phase ($P4_2/n$ phase, the first row), pyrochlore impurity (the second row), and impurity with $Pnma$ symmetry (the third row). For sample with $x = 2.0$, the tick marks show possible Bragg reflection positions of the main perovskite phase ($P4_2/n$ phase, the first row) and impurity with $Pnma$ symmetry (the second row).

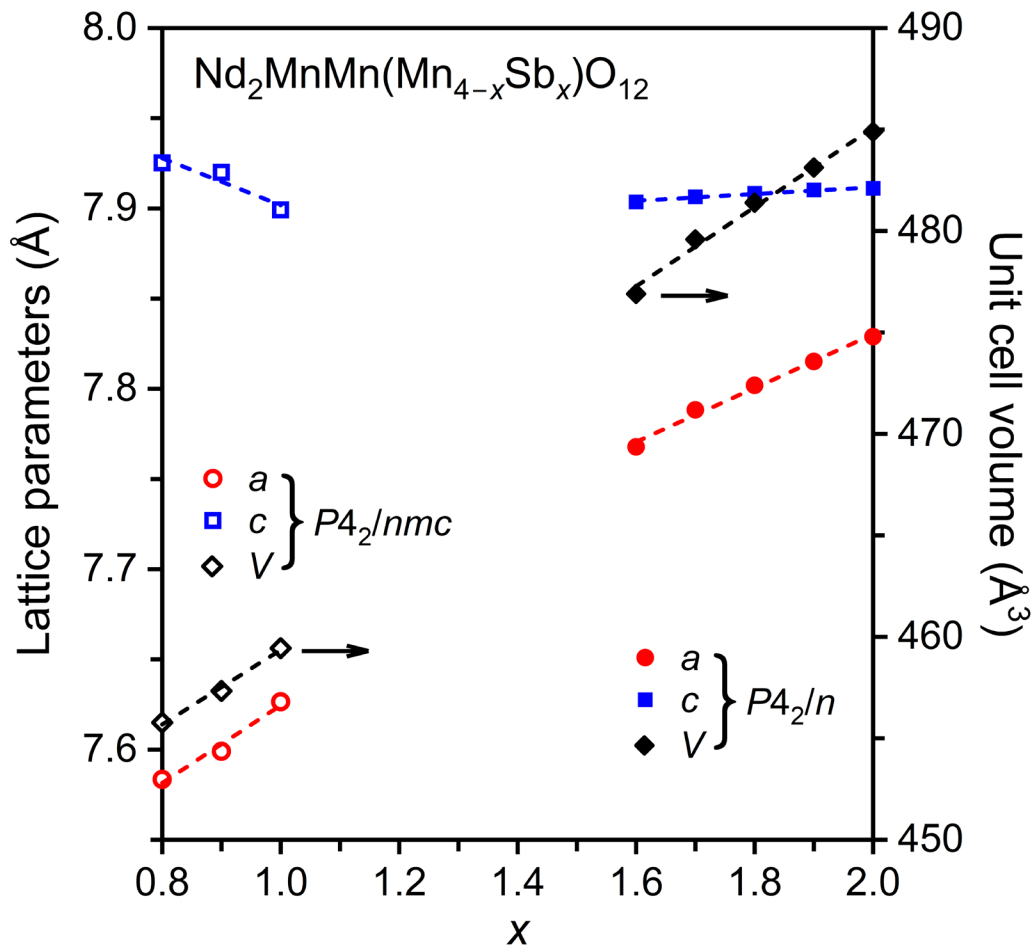


Fig. S6. Compositional dependence of the lattice parameters (a and c : the left-hand axis) and unit cell volume (the right-hand axis) of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $0.8 \leq x \leq 1.0$ and $1.6 \leq x \leq 2.0$ from synchrotron XRPD data at $T = 295$ K. Broken lines are linear fits.

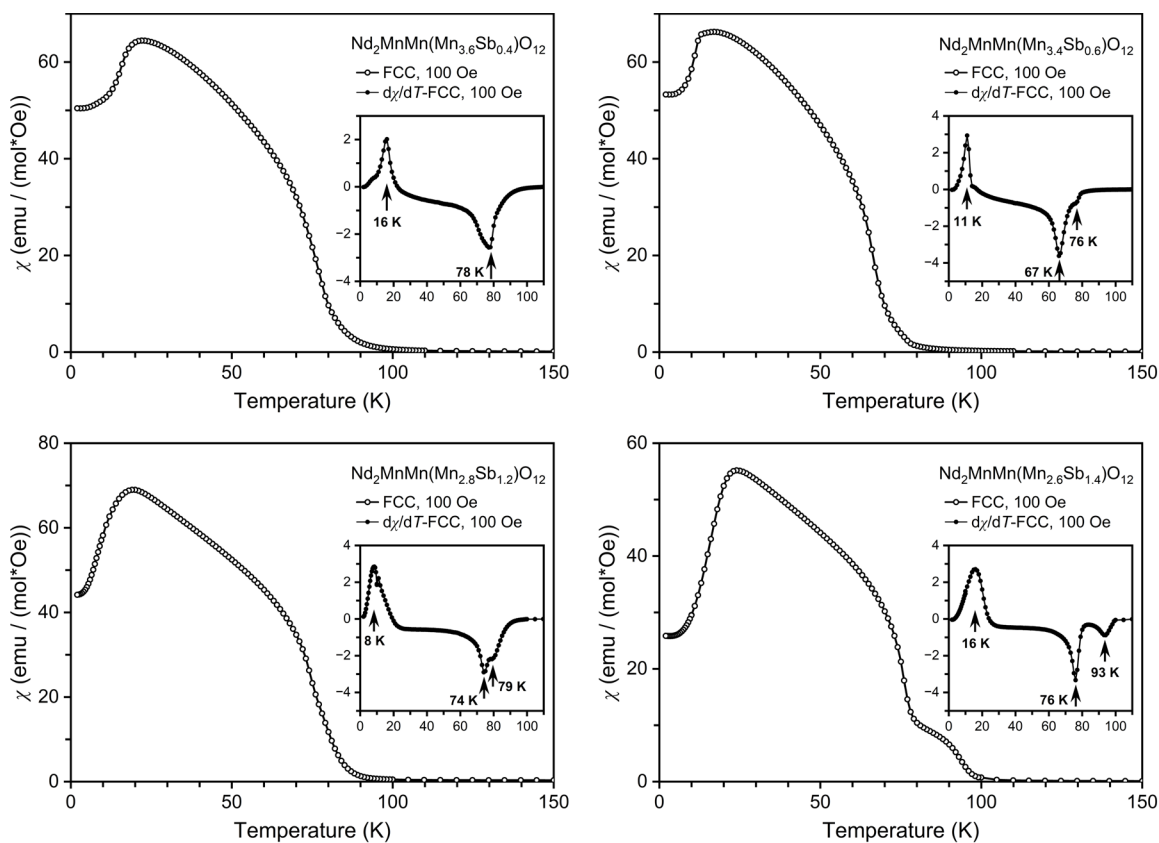


Fig. S7. FCC dc magnetic susceptibility ($\chi = M/H$) curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 0.4, 0.6, 1.2$, and 1.4 measured at 100 Oe. The inset shows 100 Oe FCC $d\chi/dT$ versus T curves.

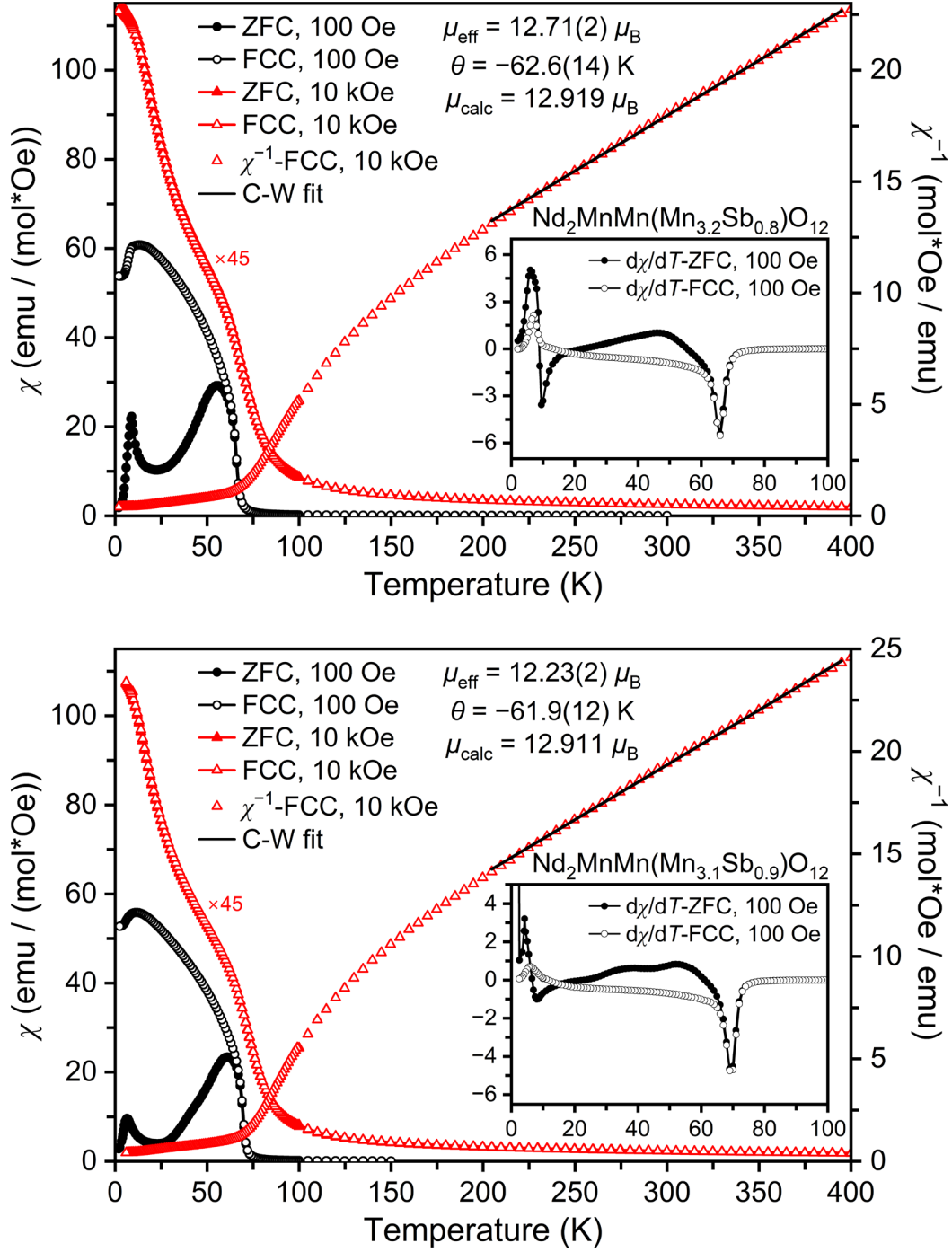


Fig. S8. ZFC (filled symbols) and FCC (empty symbols) dc magnetic susceptibility ($\chi = M/H$) curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 0.8$ and 0.9 measured at 100 Oe (black, circles) and 10 kOe (red, triangles). The black line gives the Curie-Weiss fit (C-W fit) based on the FCC χ^{-1} versus T curve at 10 kOe. The inset shows 100 Oe ZFC and FCC $d\chi/dT$ versus T curves.

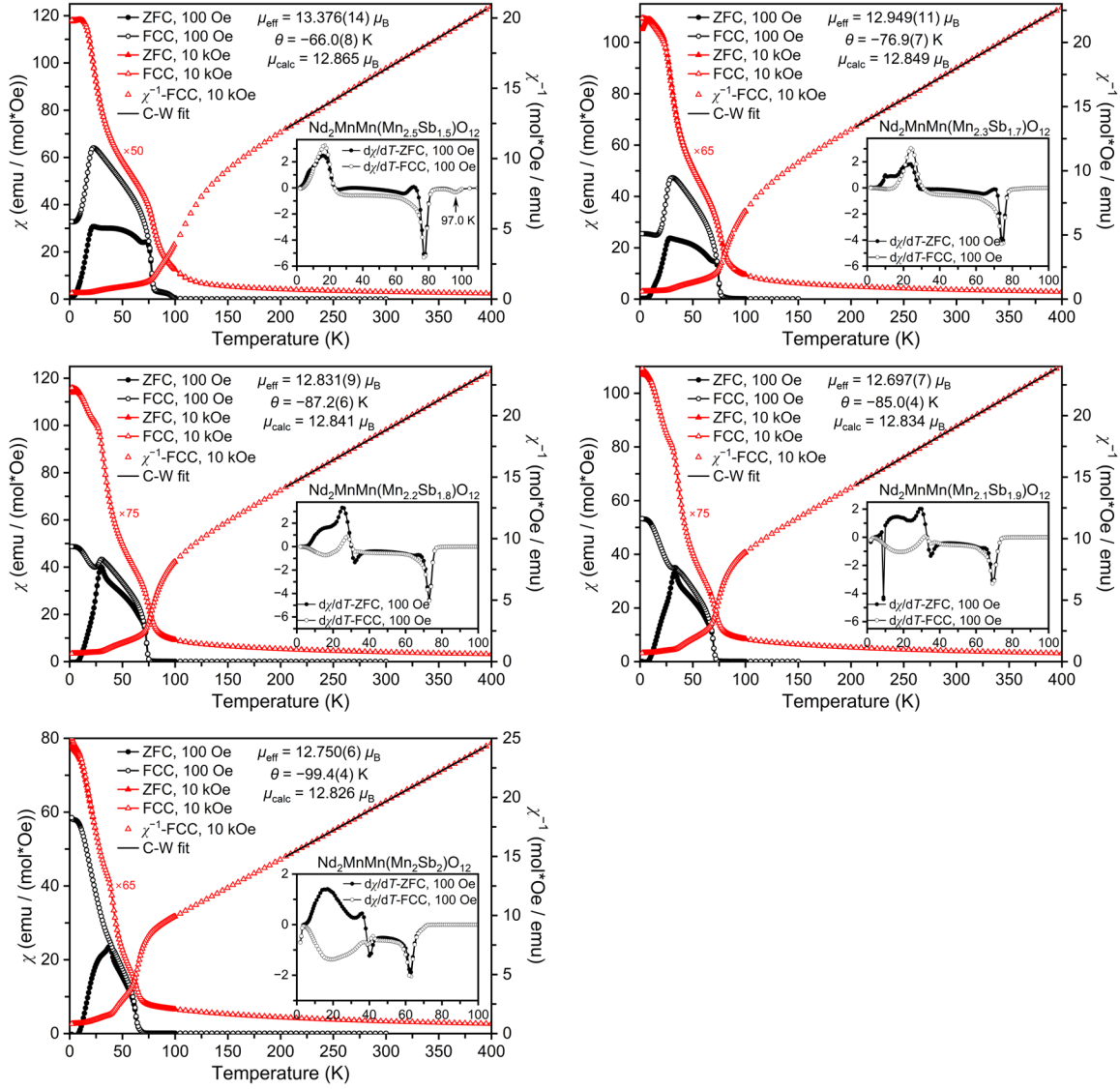


Fig. S9. ZFC (filled symbols) and FCC (empty symbols) dc magnetic susceptibility ($\chi = M/H$) curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.5, 1.7, 1.8, 1.9,$ and 2.0 measured at 100 Oe (black, circles) and 10 kOe (red, triangles). The black line gives the Curie-Weiss fit (C-W fit) based on the FCC χ^{-1} versus T curve at 10 kOe. The inset shows 100 Oe ZFC and FCC $d\chi/dT$ versus T curves.

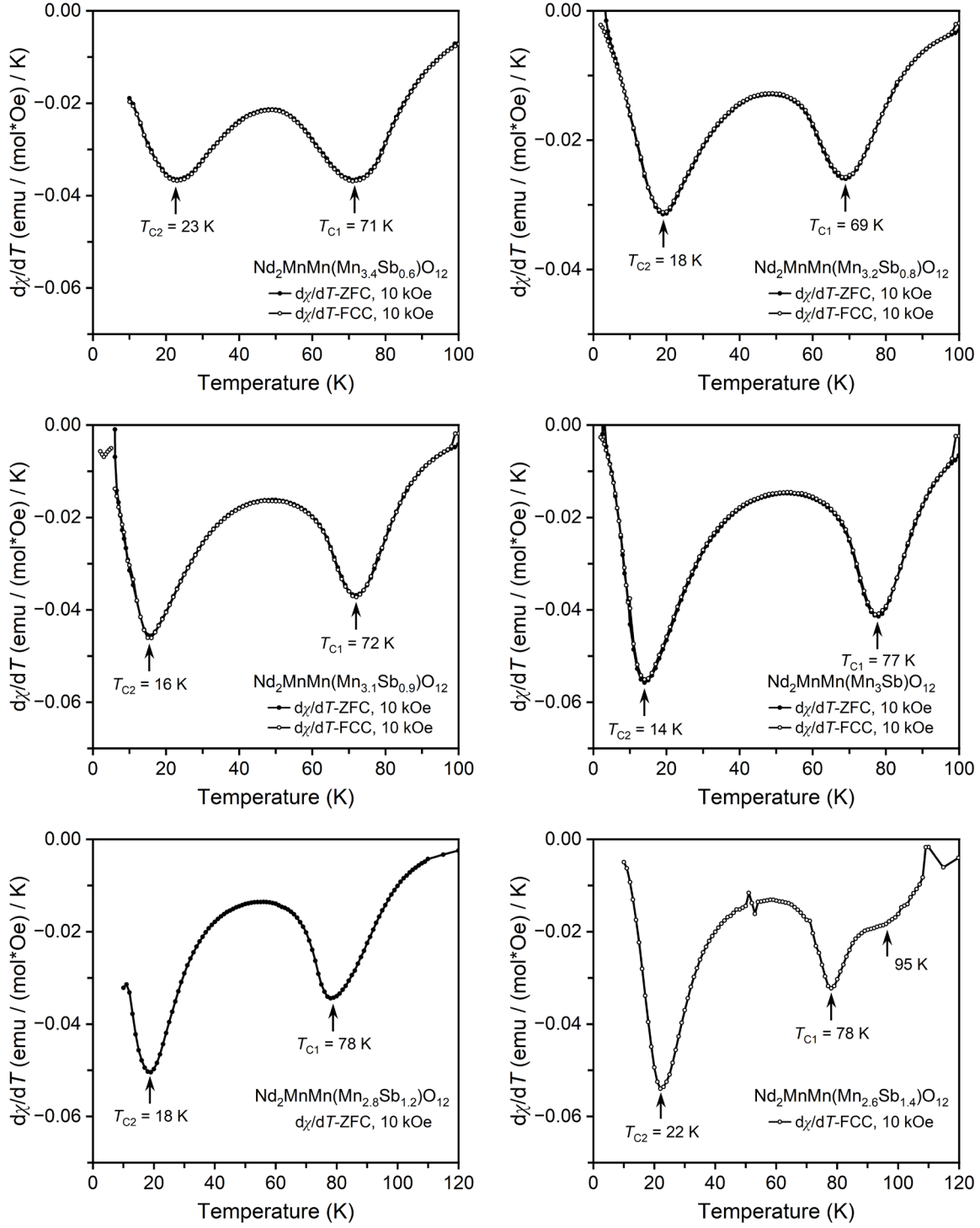


Fig. S10. 10 kOe ZFC (filled symbols) and FCC (empty symbols) $d\chi/dT$ versus T curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 0.6, 0.8, 0.9, 1.0, 1.2, \text{ and } 1.4$.

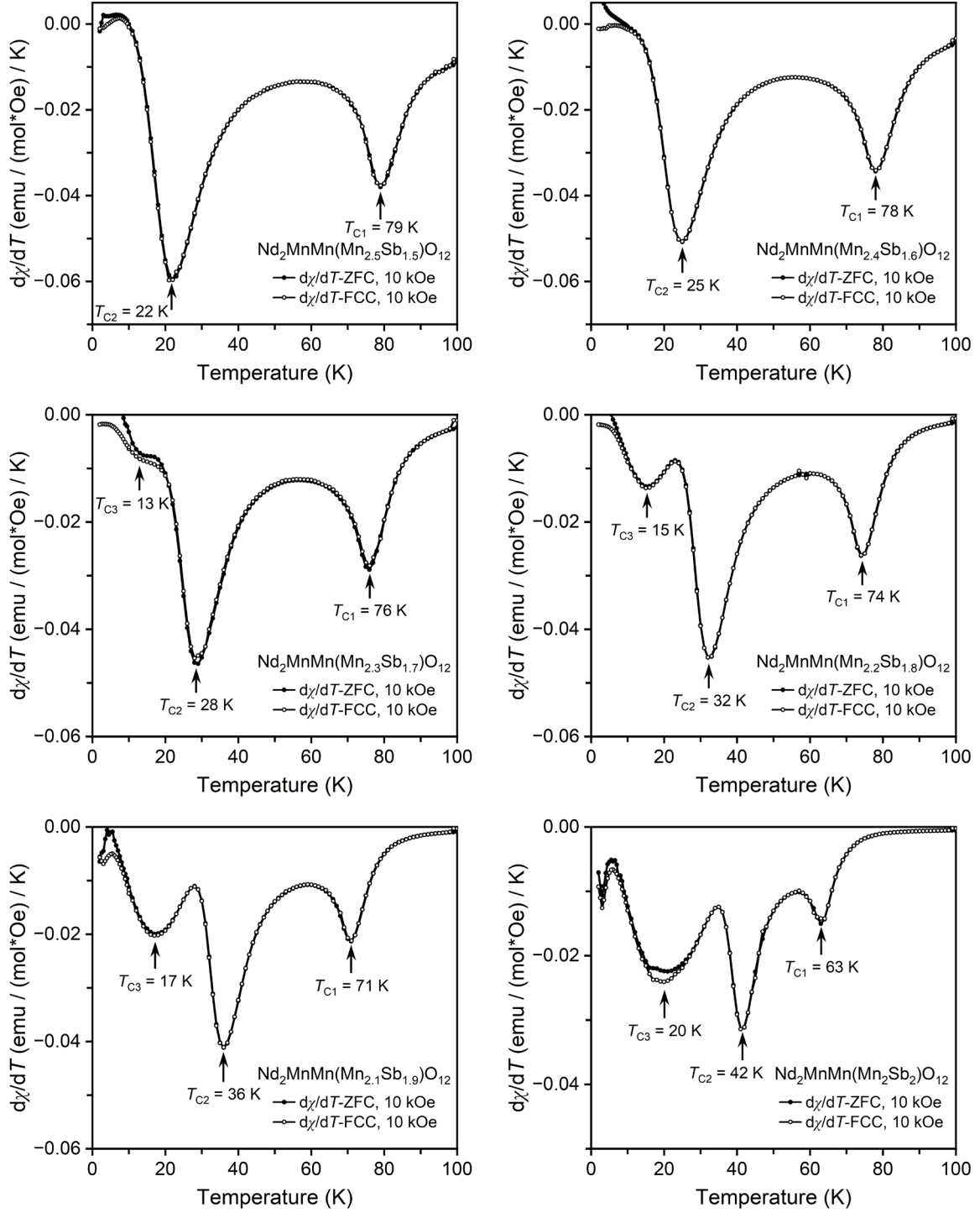


Fig. S11. 10 kOe ZFC (filled symbols) and FCC (empty symbols) $d\chi/dT$ versus T curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $1.5 \leq x \leq 2.0$.

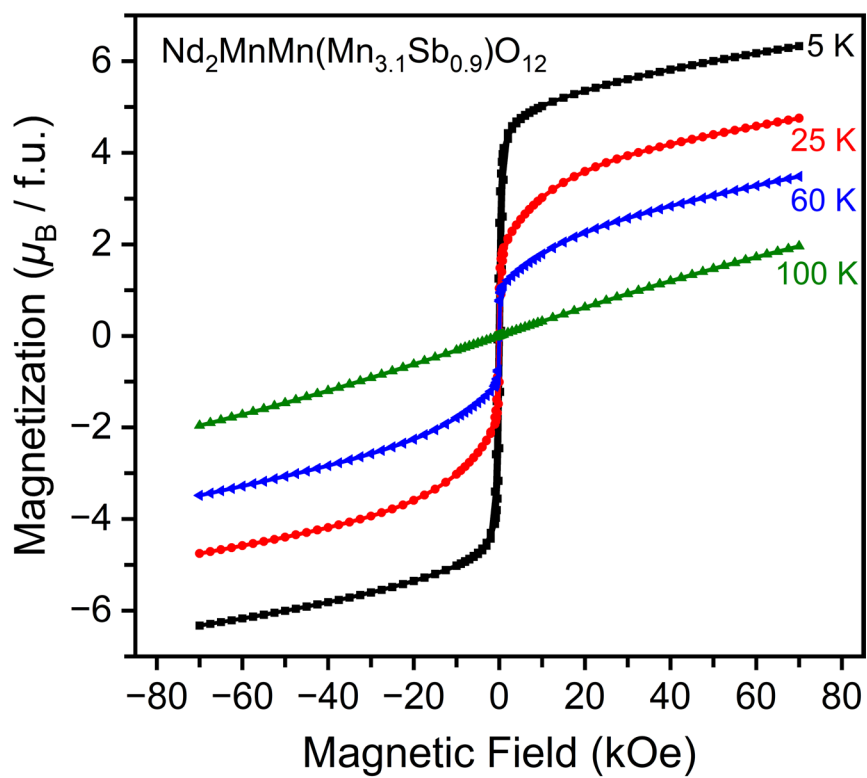
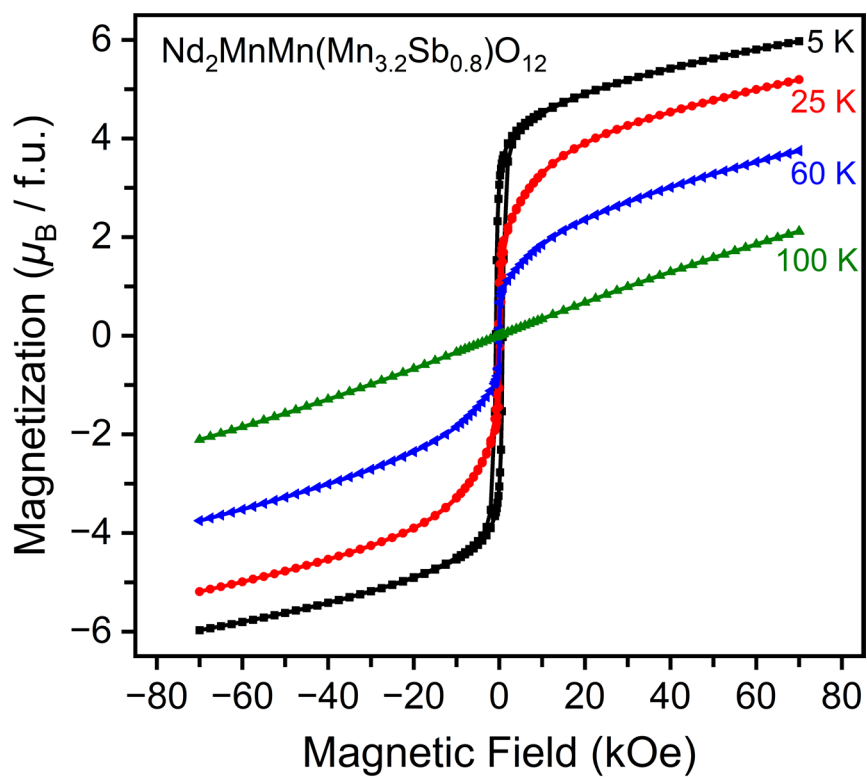


Fig. S12. M versus H curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 0.8$ and 0.9 at different temperatures.

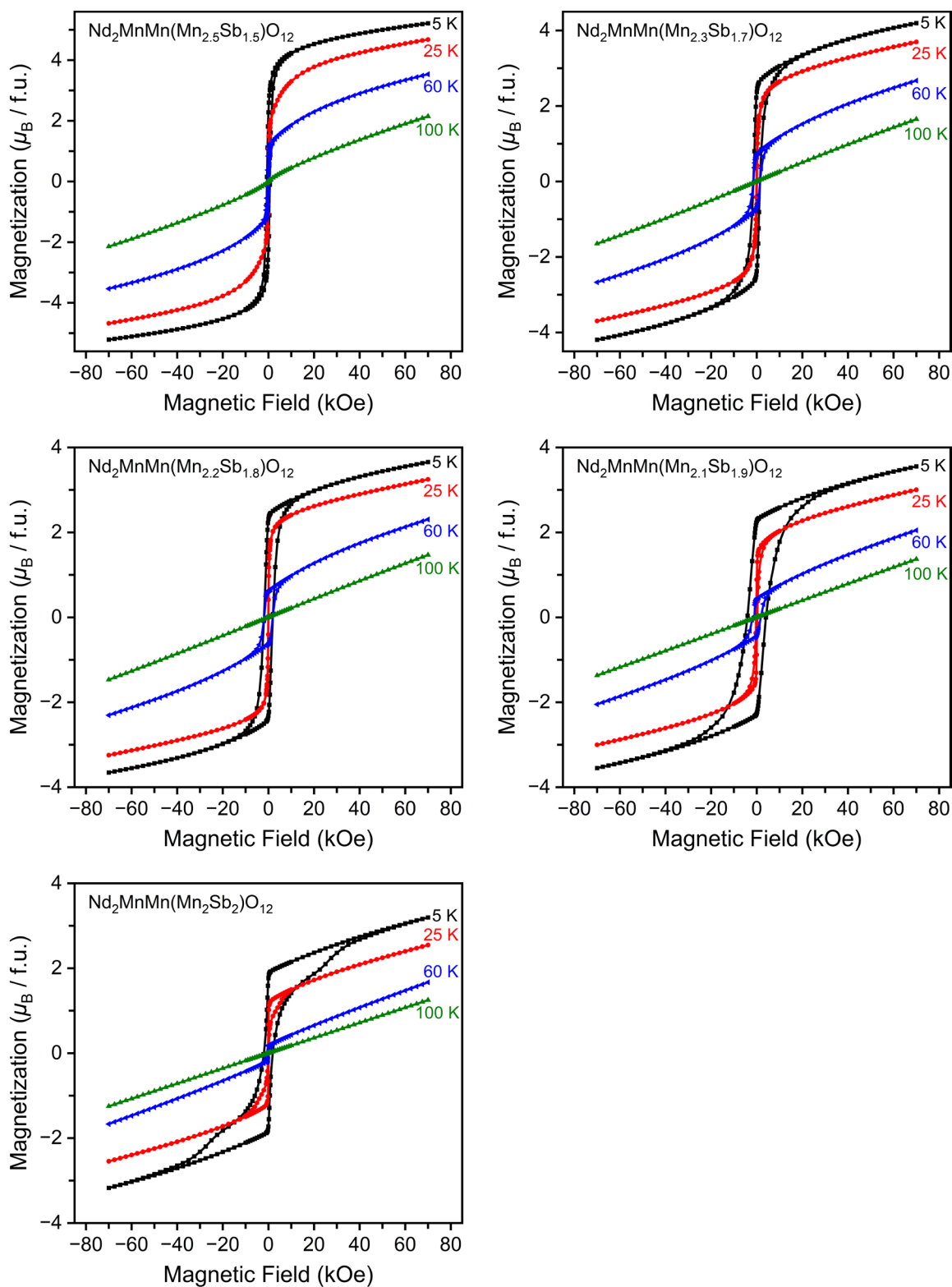


Fig. S13. M versus H curves of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.5, 1.7, 1.8, 1.9$, and 2.0 at different temperatures.

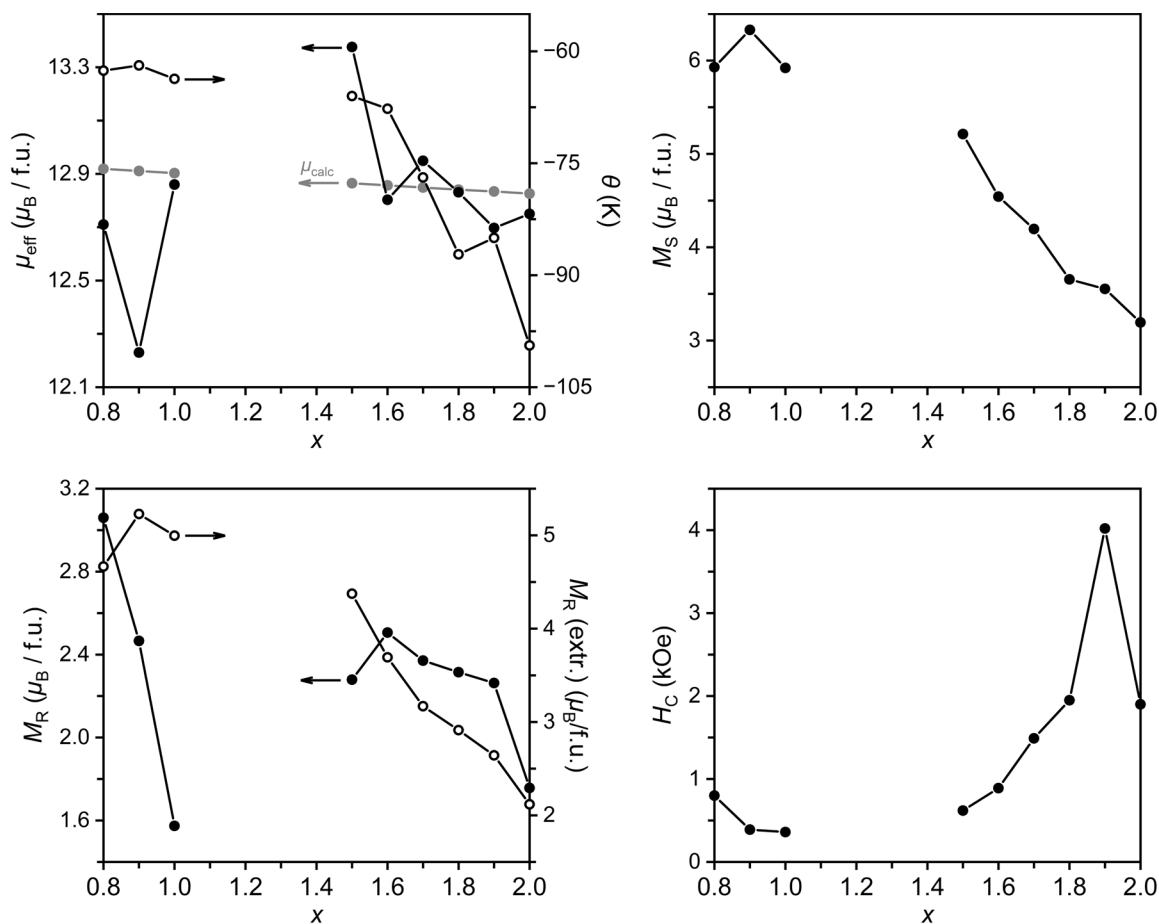


Fig. S14. Compositional dependence of the effective paramagnetic moment μ_{eff} , calculate paramagnetic moment μ_{calc} , weiss constant θ , magnetization value M_S , remnant magnetization M_R , extrapolation of remnant magnetization $M_R(\text{extr.})$, coercive field H_C in $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ solid solutions for $0.8 \leq x \leq 1.0$ and $1.5 \leq x \leq 2.0$.

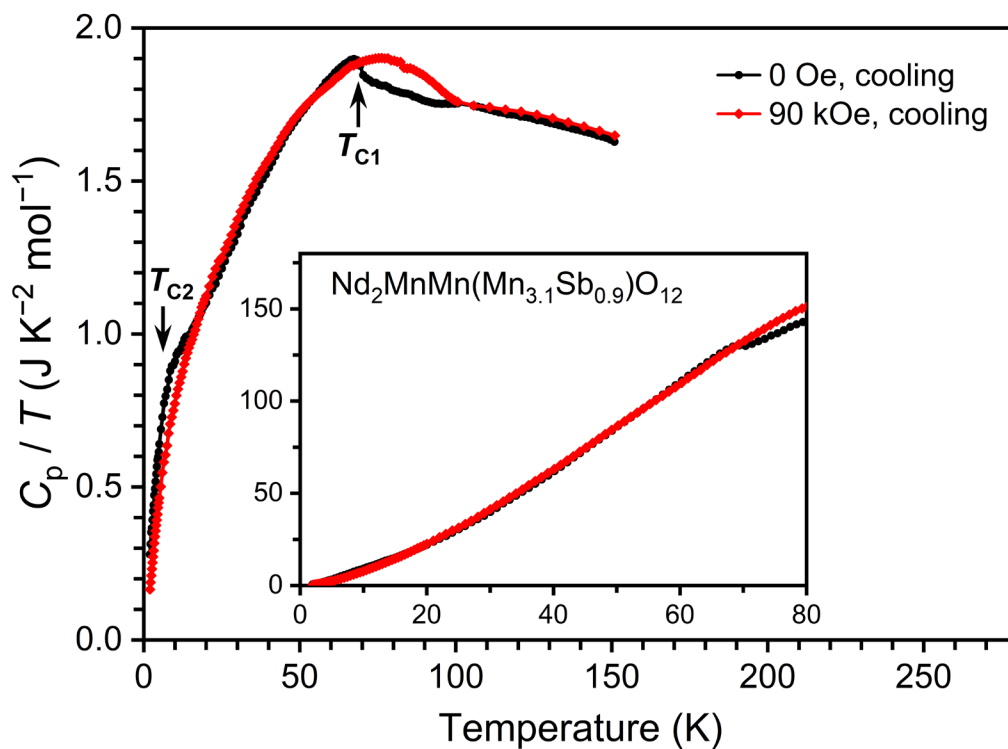
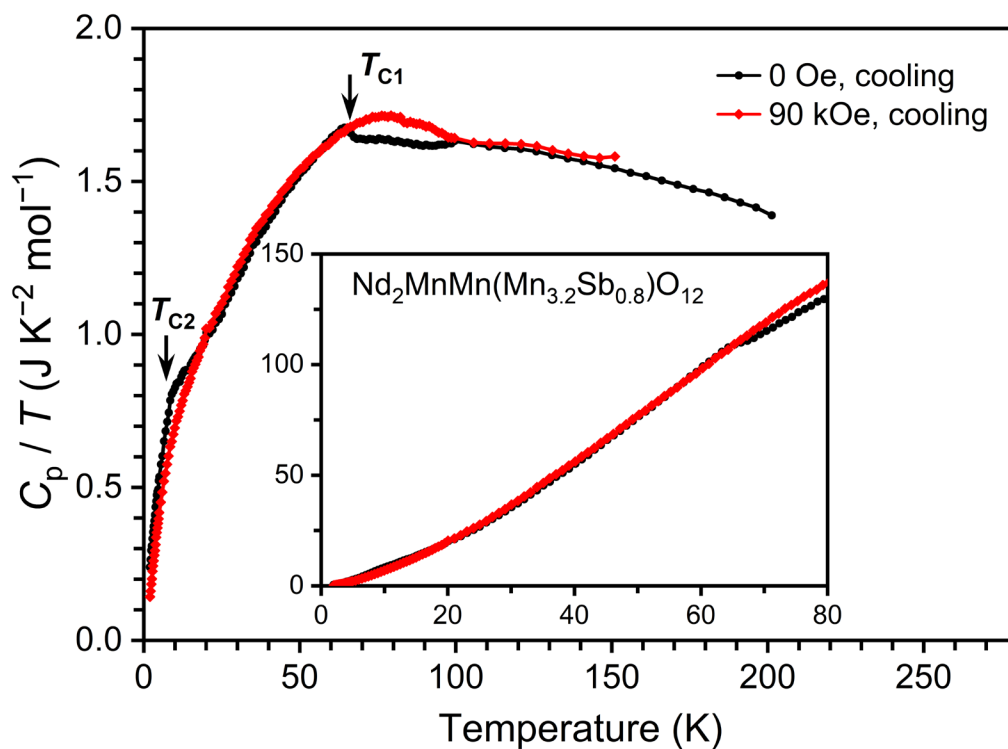


Fig. S15. Specific heat data of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 0.8$ and 0.9 , plotted as C_p/T versus T . Measurements were performed on cooling at $H = 0$ Oe and 90 kOe. Insets present the C_p (in $\text{J K}^{-1} \text{mol}^{-1}$) versus T curves.

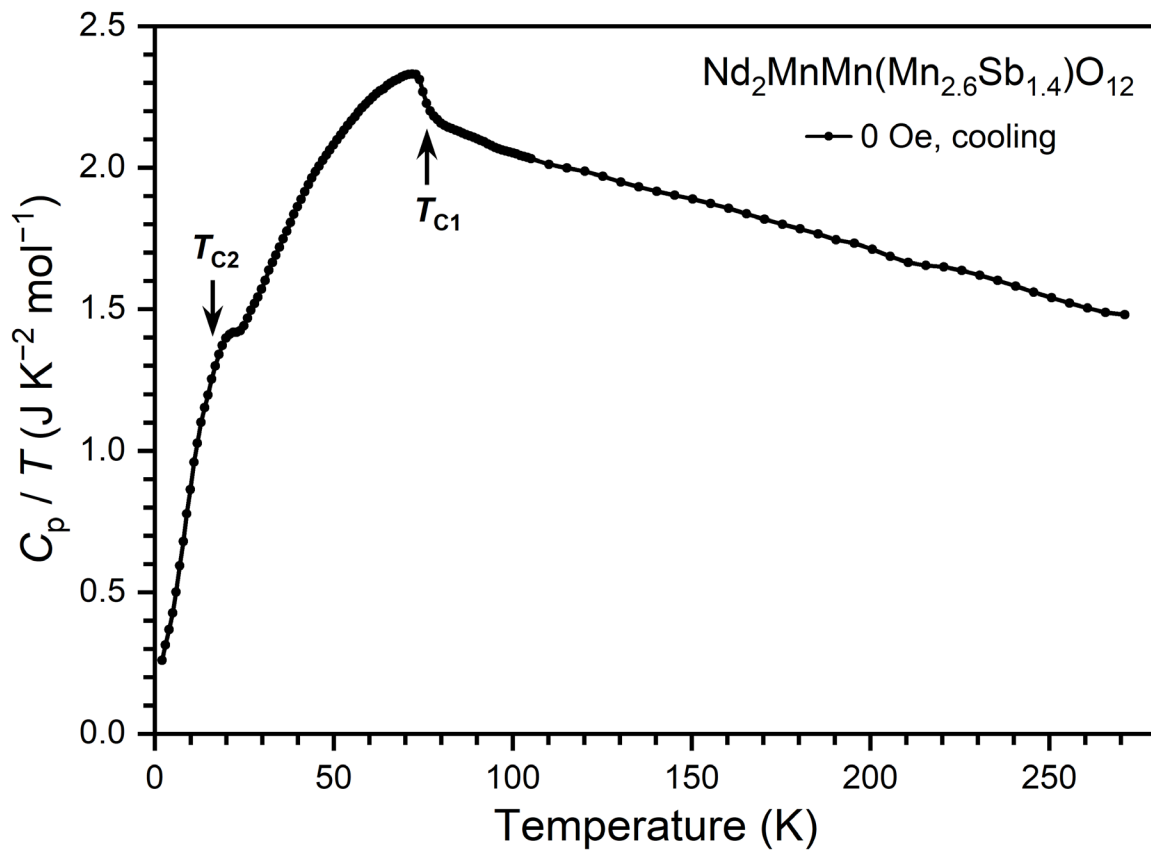


Fig. S16. Specific heat data of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.4$, plotted as C_p/T versus T . Measurements were performed on cooling at $H = 0$ Oe.

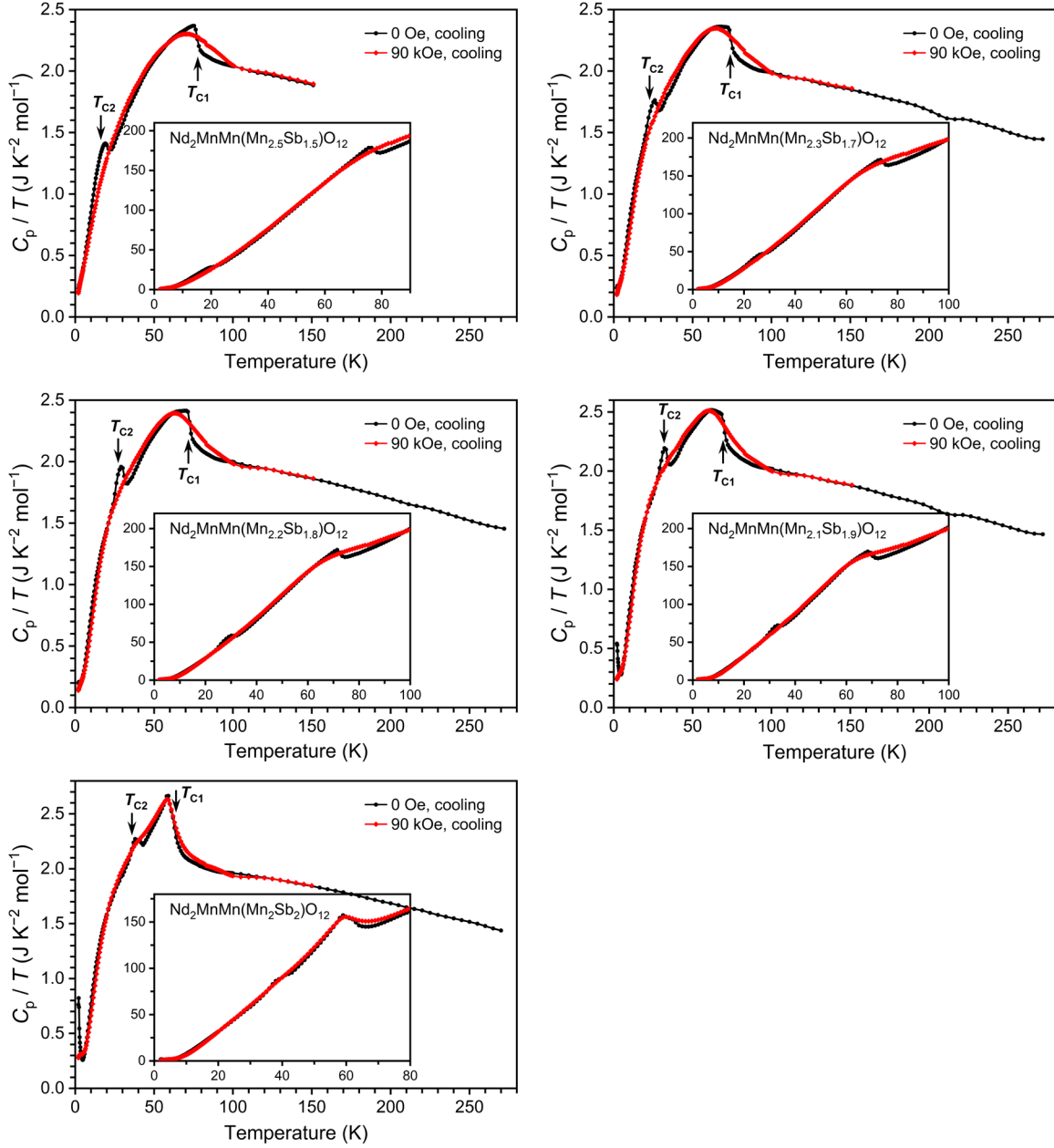


Fig. S17. Specific heat data of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.5, 1.7, 1.8, 1.9,$ and 2.0 , plotted as C_p/T versus T . Measurements were performed on cooling at $H = 0$ Oe and 90 kOe. Insets present the C_p (in $\text{J K}^{-1} \text{mol}^{-1}$) versus T curves. The rise of the C_p/T values at low temperatures in the $x = 1.9$ and 2.0 samples could be caused by the presence of an unknown impurity.

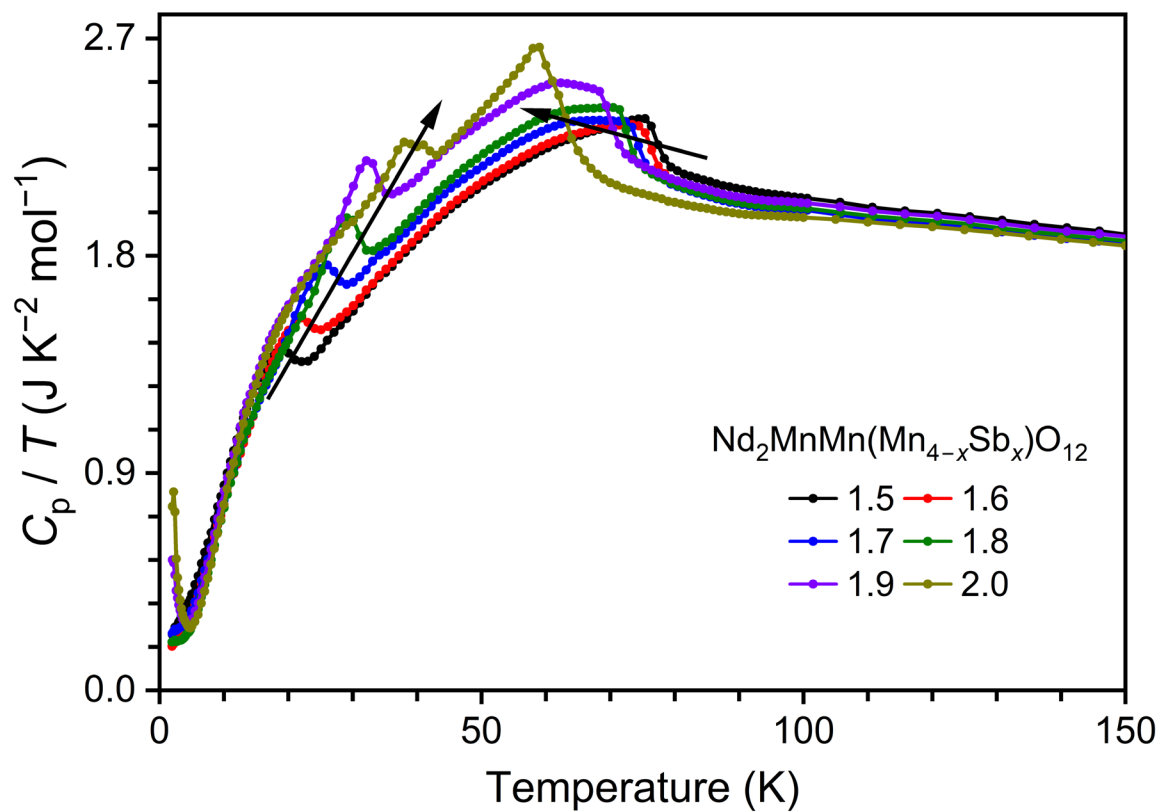


Fig. S18. Specific heat data of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $1.5 \leq x \leq 2.0$, plotted as C_p/T versus T . Measurements were performed on cooling at $H = 0$ Oe.

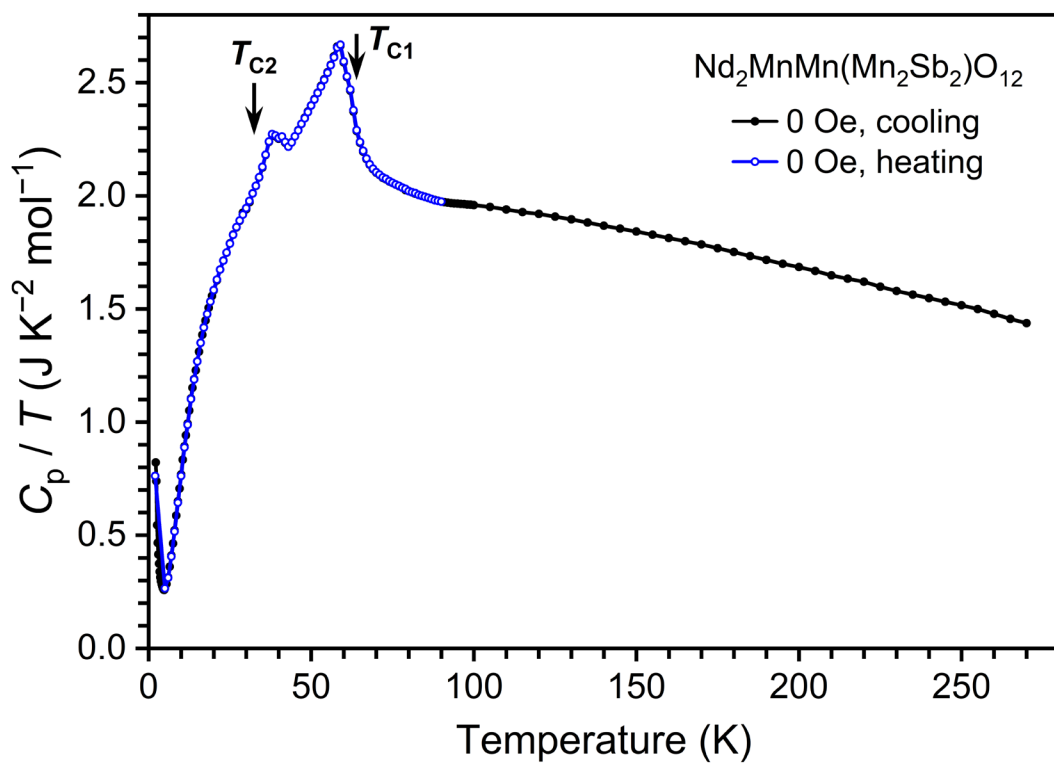
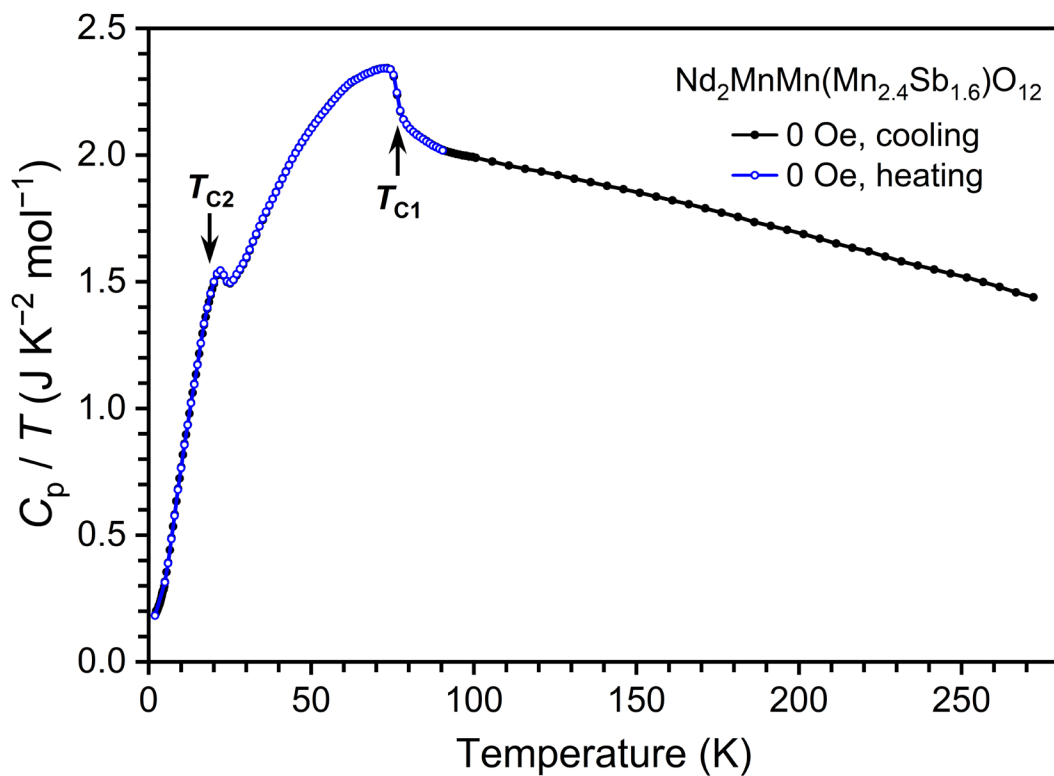


Fig. S19. Specific heat data of $\text{Nd}_2\text{MnMn}(\text{Mn}_{4-x}\text{Sb}_x)\text{O}_{12}$ with $x = 1.6$ and 2.0 , plotted as C_p/T versus T . Measurements were performed on cooling and heating at $H = 0$ Oe.