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High-pressure high-temperature synthesis of magnetic perovskite $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$



Chiara Coppi^{1,2}✉, Fabio Orlandi³, Francesco Mezzadri^{1,2}, Giuseppe Allodi⁴, Andrea Migliori⁵, Riccardo Cabassi¹, Francesco Cugini⁴, Massimo Solzi⁴, Giovanna Trevisi¹, Marzio Rancan⁶, Lidia Armelao^{7,8}, Edmondo Gilioli¹ & Davide Delmonte¹

Complex perovskite oxides stabilized under high-pressure conditions constitute a rich playground for material science thanks to their multifunctional properties. Here we present the synthesis of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$, obtained under isotropic high-pressure/high-temperature conditions. The compound crystallizes in the orthorhombic Pbam space group with $a = 5.57960(16)$ Å, $b = 11.2374(3)$ Å, $c = 7.6603(2)$ Å. Disorder between Cu and Mn cations at the B site causes a significant interplay between electric and magnetic properties. Although a long-range magnetic order is not observed in neutron diffraction, $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ displays a ferromagnetic-like transition at 330 K confined at the local scale and thermal-activated semiconductive behavior. At lower temperatures, the partial electronic localization on the Mn site changes the transport mechanism leading to 3D variable range hopping conductivity and determines the formation of an antiferromagnetic ordering at about 30 K. The presence of ferromagnetic-like room temperature state makes this material intriguing as a starting point for advanced multifunctional devices.

Perovskites (ABO_3), due to their wide tolerance to chemical substitutions and structural distortions, represent a promising and versatile playground for the study of multifunctional inorganic materials. Indeed, by substituting different ions on the A and the B sites, it is possible to tune the physical properties, like the presence of multiple ferroic orders (ferromagnetism, ferroelectricity, ferroelasticity, ferrotoroidicity)¹, spin-polarized carriers², magnetostriction³, magnetoresistance⁴, photocatalytic and photovoltaic effect⁵ just to name few. The versatile character of the perovskite structure, allowing it to retain stability even for Goldschmidt tolerance factor values far from 1⁶, allows to obtain low crystallographic symmetries and, in a few cases, the coexistence in a single phase of competing phenomena, like magnetism and ferroelectricity. An extension of this stability range can be achieved thanks to high-pressure/high-temperature (HP/HT) syntheses, able to stabilize highly distorted and metastable compounds to ambient conditions, particularly considering the high density of the perovskite structure^{7–11}.

Bi-based double perovskites ($\text{Bi}_2\text{B}'\text{B}''\text{O}_6$) constitute a system showing exotic properties, where the insertion of the Bi^{3+} ion at the A site can induce local distortions and promote the formation of a net electric dipole in the structure, thanks to its stereochemical effect^{12–14}, as reported for instance in $\text{BiCr}_{0.95}\text{Fe}_{0.05}\text{O}_3$ ¹⁵. The B' or B'' sites are usually occupied by different transition metals (TM) with an incomplete d-shell giving rise to super-exchange interactions, thus allowing the possibility for different types of magnetic orderings according to the Goodenough-Kanamori-Anderson (GKA) rules for octahedral coordination of metallic cations^{16–18}. For example, in the highly distorted double perovskite $\text{Bi}_2\text{NiMnO}_6$, in which Ni^{2+} and Mn^{4+} ions are ordered in a rock-salt configuration, the Ni^{2+} -O-Mn⁴⁺-O-Ni²⁺ magnetic path leads to ferromagnetism with $T_C = 140$ K¹⁹. By properly choosing the B' and B'' ions, it is possible to control multiple functionalities, opening the route to a wide variety of new applications, such as in spintronic or energy storage devices. A comprehensive example of physical properties tunability is represented by $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ solid-

¹Institute of Materials for Electronics and Magnetism, National Research Council (IMEM-CNR), Parco Area delle Scienze 37/A, I-43124 Parma, Italy. ²Department of Chemical Sciences, Life and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17/A, I-43124 Parma, Italy. ³ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, OX11 0QX, UK. ⁴Department of Mathematical, Physical and Computer Sciences, University of Parma, Parco Area delle Scienze 7/A, I-43124 Parma, Italy. ⁵CNR-IMM Sez. Bologna, Via Piero Gobetti 101, 40129 Bologna, Italy. ⁶Institute of Condensed Matter Chemistry and Technologies for Energy (ICMATE), National Research Council (CNR), c/o Department of Chemistry, University of Padova, via F. Marzolo 1, 35131 Padova, Italy. ⁷Department of Chemical Sciences, University of Padova, via F. Marzolo 1, Padova, Italy. ⁸Department of Chemical Sciences and Materials Technologies (DSCTM), National Research Council (CNR), Piazzale A. Moro 7, 00185 Roma, Italy. ✉e-mail: chiara.coppi@cnr.it

solution, in which by varying the stoichiometry ratio between Fe and Mn^{20–27} till the two extensively studied functional endmembers BiFeO₃^{28–34} and BiMnO₃^{35–37} it is possible to modify the magnetic orders type and onset temperature as well as to module their ferroelectric state even reaching multiferroicity. Recent research efforts have been increasingly focused on Bi-based perovskites, aiming to enhance their quality and performance^{38–41}. Unfortunately, the usually low critical temperature hampers the technological use of many promising multifunctional perovskites. To overcome this limitation, chemical substitutions in known perovskite systems must be explored to develop novel materials better suited for technological applications.

In this work, we present the HP/HT synthesis of BiCu_{0.4}Mn_{0.6}O₃ (BCMO), a Bi-based perovskite. The composition has been chosen to achieve a ferromagnetic/ferroelectric state. Indeed, the stereochemically-active Bi ion at A site might introduce a spontaneous polarization in the system, while Cu-O-Mn superexchange interaction might lead to a ferromagnetic order in case of 180 degrees angle between the TMs. The insertion of Cu²⁺ and Mn⁴⁺ in the B site of the perovskite lattice implies values of the Goldschmidt factor well below unity⁴², requiring the use of HP/HT techniques to stabilize this phase at ambient condition^{43–45}. Here, we discuss in detail the structural, magnetic, and electrical proprieties of this material, highlighting how the disorder on the B site can be used to obtain a ferromagnetic-like state in ambient conditions.

Results

Synthesis conditions

BCMO was synthesized at 4 GPa and 1000 °C, and the best yield was obtained for a reaction time of 0.5 h. The pressure required to stabilize BCMO perovskite is slightly lower compared to the 6 GPa needed for the

synthesis of BiFe_{0.5}Mn_{0.5}O₃²⁴. Longer solid-state reaction time leads to the degradation of the perovskite phase, while shorter duration times seem to promote undesired phases (Supplementary Fig. 1).

Morphology, chemical composition, and preliminary structural analysis

Scanning electron microscopy (SEM) measurements were performed to study the morphology and the stoichiometry of BCMO in imaging and quantitative energy dispersive spectroscopy (EDS) analysis modes, both on grounded (Fig. 1) and bulk samples (Supplementary Fig. 2). Quite large super-micrometric multi-faceted grains are visible (Fig. 1a, b), while on the surface of larger crystallites small sub-micrometric clusters are present, probably of the same nature as the intra-grains inhomogeneities observed in the bulk form (Supplementary Fig. 2b). Point EDS measurements, as the one shown in Fig. 1d and acquired on the area indicated with the yellow spot in Fig. 1c, indicated a discrepancy of the measured Cu:Mn stoichiometry ratio with respect to the predicted 1:1, around 0.6:0.4, suggesting the impurities observed in the diffraction measurement are Cu-rich compounds.

Transmission electron microscopy (TEM) analyses on BCMO powders are reported in Fig. 2. Crystalline sub-micrometric grains are visible in scanning-TEM (STEM) high-angle annular dark-field (HAADF) (Fig. 2a) imaging modes. The single fragments contain more than one crystallographic phase, as the contrast cannot be attributed to thickness differences. Coherently with the SEM-EDS analyses, impurities, probably related to copper oxide-rich compounds, are also present at the micrometric level. STEM-EDS analyses were done in homogeneous areas, and the stoichiometry ratio of Bi:Cu:Mn is coherent with the previously reported SEM analysis, confirming a Cu deficiency. Selected area electron diffraction (SAED) patterns were collected in different zone axes of small grains, and

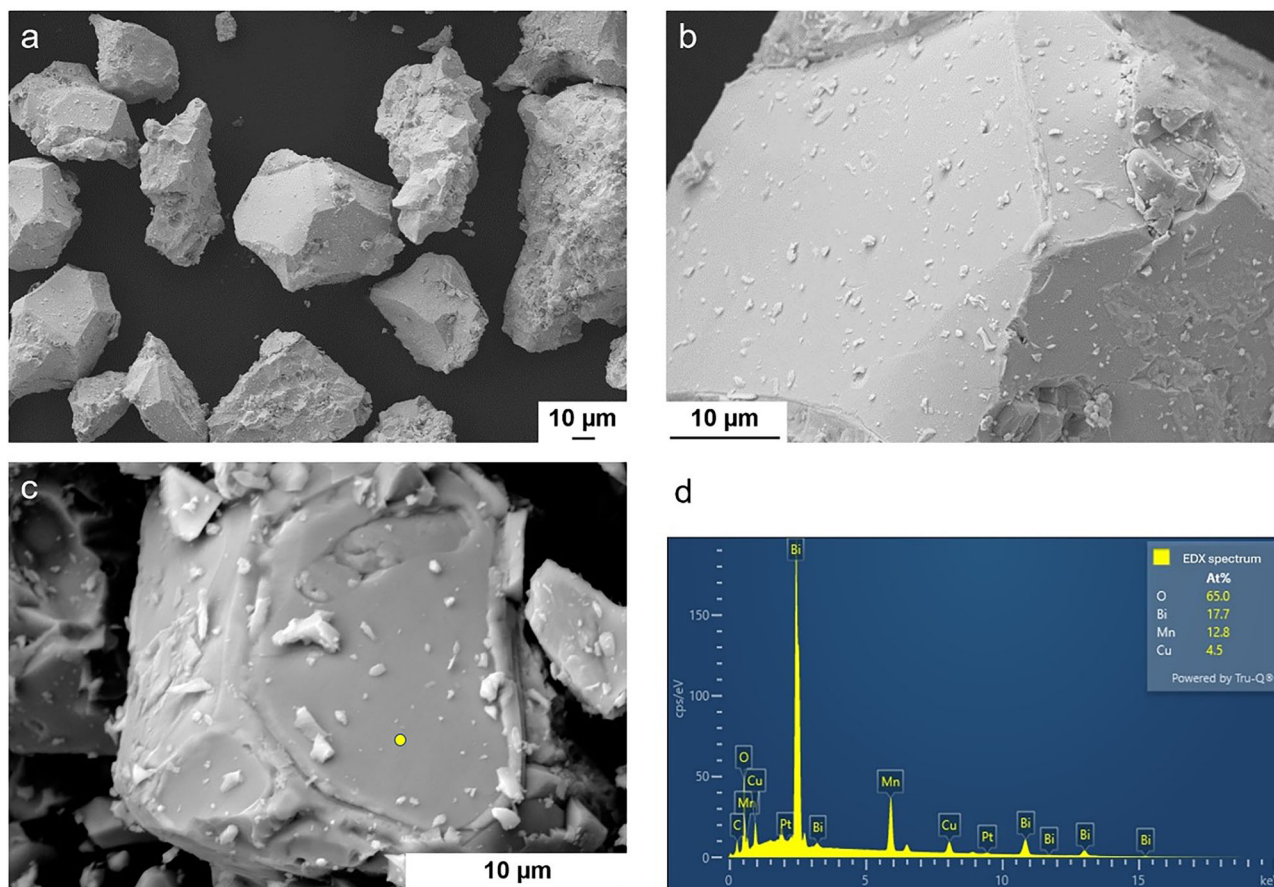
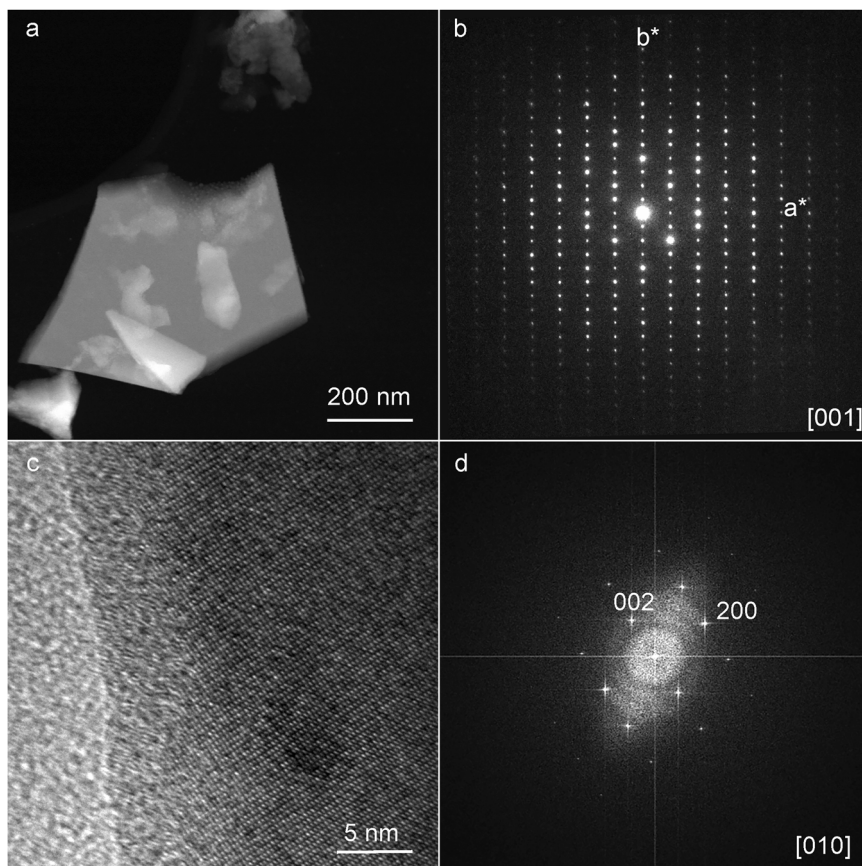


Fig. 1 | Morphology and chemical composition of BiCu_{0.4}Mn_{0.6}O₃. Scanning electron microscopy images (a–c) and punctual energy dispersive spectroscopy analysis of BiCu_{0.4}Mn_{0.6}O₃ powder on the yellow spot reported in (c) with the related spectrum (d).

Fig. 2 | Transmission electron microscopy of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$. Transmission electron microscopy (TEM) analyses on $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ in different modes: high-angle annular dark-field scanning-TEM (a), [100] Selected area electron diffraction (b), high resolution-TEM taken on the [010] zone axis (c), and the relative fast Fourier transform (d).



one, taken along the [010] direction, is reported in Fig. 2b. All the observed reflections can be indexed with an orthorhombic cell with lattice parameters $a \approx 5.58 \text{ \AA}$, $b \approx 11.23 \text{ \AA}$, $c \approx 7.66 \text{ \AA}$. These values can be considered as the result of a distortion from the ideal simple cubic perovskite lattice parameter $a_{\text{sp}} \approx 3.8 \text{ \AA}$, particularly with $a \approx \sqrt{2}a_{\text{sp}}$, $b \approx 2\sqrt{2}a_{\text{sp}}$, $c \approx 2a_{\text{sp}}$. The Fourier-transform of high-resolution HR-TEM image taken on [010] zone axis and reported in Fig. 2d, confirms the lattice parameters previously estimated via SAED.

Room temperature nuclear structure

The crystal structure of BCMO was solved by the combined use of powder X-ray diffraction (PXRD) and powder neutron diffraction (PND) data. The collected diffraction peaks, both with X-rays and neutrons sources, are characterized by a quite large profile shape, with a full-width half maximum (FWHM) of around 0.22° for the most intense PXRD reflection, a feature likely related to the defective nature of the sample often reported in HP/HT-obtained materials^{46,47}. The observed reflections are compatible with the lattice parameters calculated from SAED. The space group (s.g) symmetry was determined as Pbam (#55), consistent with the systematic extinctions, namely $0kl$ with $k = 2n + 1$ and $h0l$ with $h = 2n + 1$, observed both in the XRD and ND patterns. The reason for the choice of the centrosymmetric Pbam s.g. with respect to the associated non-centrosymmetric Pbam2 one is due to the lack of discrimination with powder diffraction techniques between the hkl and $-h-k-l$ reflections, and the reduction of the symmetry does not provide significant improvements of the agreement factors despite the increased number of refinable parameters. In the diffraction data, two main spurious phases were observed: bismuth oxycarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ (ICSD cod. 202767) and copper (II) oxide CuO (ICSD cod. 16025).

The refinement of the crystallographic model was carried out with the Rietveld method in Jana2020⁴⁸ by the combined use of both PXRD and PND data. Considering the defectivity of HP/HT samples, to reduce the number of free parameters during the refinement process, some constraints have

been introduced. The occupancy of both bismuth and oxygen species was fixed to 1 since the refined occupancy was compatible with this value within error, and the sum between the relative occupancy of the TM at the B site was constrained to unity. Moreover, isotropic thermal displacement U_{iso} parameters were used for all the atomic species. The value for the R_{wp} parameter, around 5%, confirms a reliable model obtained for BCMO, as can also be appreciated from the Rietveld plot reported in Fig. 3. The obtained structural parameters for BCMO are reported in Table 1, with lattice parameters refined to $a = 5.57960(16) \text{ \AA}$, $b = 11.2374(3) \text{ \AA}$, $c = 7.6603(2) \text{ \AA}$. Figure 4 shows a drawing of the crystal structure, which is characterized by a PbZrO_3 -type distortion⁴⁹, with the bismuth ions shifted along the [111] pseudocubic direction in an up-up-down-down fashion with an $a^+a^+c^0$ tilting in Glazer notation⁵⁰ of the TMO_6 octahedra. From the Rietveld refinement of the neutron data, no cation ordering at the B site involving Mn and Cu was observed coherently with the Pbam space group, allowing only one symmetry-independent B site. The structural disorder of BCMO is also reflected in the slightly larger thermal parameters and, in turn, in the positions of oxygens species. However, a notable Cu deficiency, compared with the target composition, was observed (see Table 1), which is compatible with the segregation of the detected CuO impurity, and the Cu/Mn ratio, around 0.38/0.62, agrees with the SEM-EDS analysis. The charge neutrality of BCMO is likely maintained assuming a mixture of $\text{Mn}^{3+}/\text{Mn}^{4+}$ cations on the B site, reduction process that is frequently induced under high pressure conditions^{51–54}, since we do not observe any vacancies either on the Bi or O sites from our diffraction data. Manganese population has been confirmed to be mainly present in the 4+ valence state, also by X-ray photoelectron spectroscopy (XPS) analyses, which, however, revealed the coexistence of a minor concentration of Mn^{3+} , while copper is predominantly present as Cu^{2+} (details in Supplementary Figs. 3 and 4). The octahedral arrangement of the oxygens surrounding the TM at the B site is highly distorted, as shown in Fig. 4. This feature is coherent with the stereochemically active Bi^{3+} ion at the A site. The purity level of the perovskite

Fig. 3 | Crystal structure resolution of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$. Rietveld refinement of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ from powder X-ray diffraction (PXRD) (a) and powder neutron diffraction (PND) (b) at room temperature. The observed data (black dots), the calculated ones (red line), and their difference (yellow line) are reported. Expected reflections for $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ (orange tick marks), $\text{Bi}_2\text{O}_2\text{CO}_3$ (blue tick marks, ICSD cod. 202767), and CuO (green tick marks, ICSD cod. 16025) are shown. $R_{\text{wp}} = 5.2\%$, $R_p = 3.62\%$, $R_{\text{Obs}} = 5.30$, $R_{\text{wobs}} = 12.21$, and $\text{GOF} = 2.57$ values for PXRD, while for PND are $R_{\text{wp}} = 5.14\%$, $R_p = 3.81\%$, $R_{\text{Obs}} = 7.51$, $R_{\text{wobs}} = 12.30$, and $\text{GOF} = 3.03$.

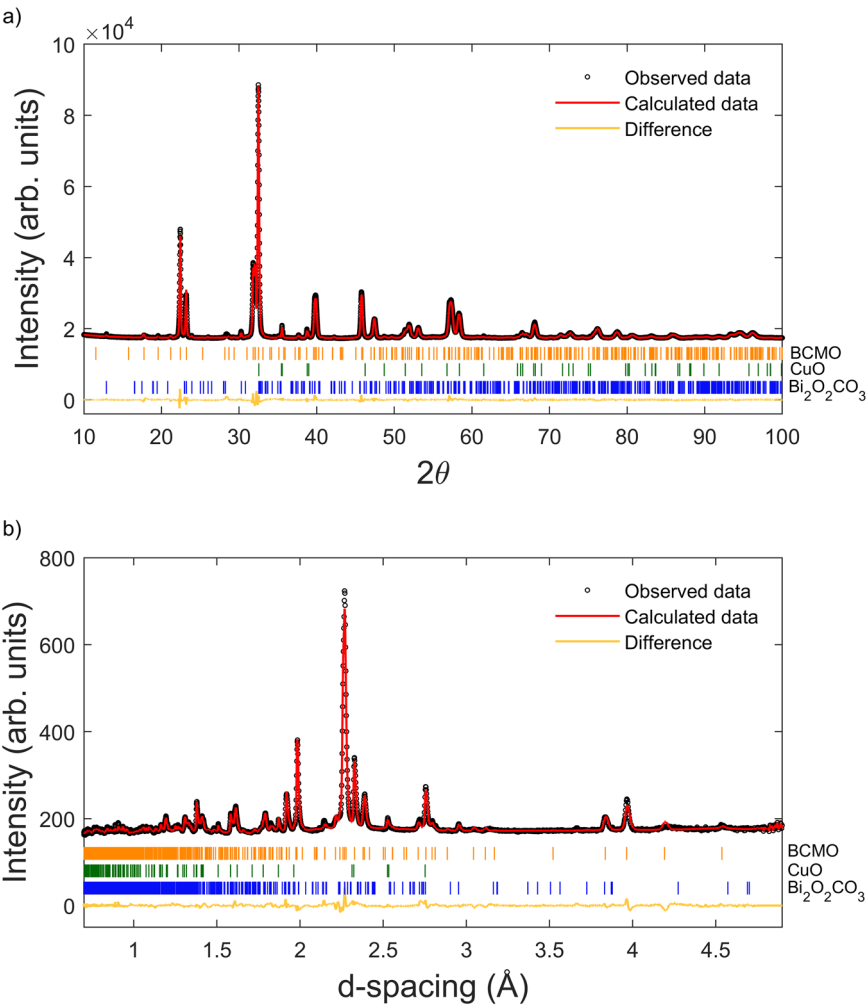


Table 1 | Refined parameters of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ unit cell

Atoms	x	y	z	Occ.	U_{iso}	Site
Bi_1	0.7487(3)	0.6194(2)	0	1	0.01867(18)	4 g
Bi_2	0.7738(3)	0.6282(2)	0.5	1	0.01867(18)	4 h
Mn	0.2320(7)	0.6325(5)	0.2484(17)	0.6166(13)	0.0083(6)	8i
Cu	0.2320(7)	0.6325(5)	0.2484(17)	0.3834(13)	0.0083(6)	8i
O_1	0	0.5	0.2003(12)	1	0.056(3)	4 f
O_2	0	0	0.2129(14)	1	0.076(3)	4e
O_3	0.4351(7)	0.7595(3)	0.2902(8)	1	0.0248(14)	8i
O_4	0.2387(13)	0.6687(9)	0	1	0.093(4)	4 g
O_5	0.1809(10)	0.5899(6)	0.5	1	0.0046(17)	4 h

Structure parameters for $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ from combined Rietveld refinement of powder X-ray diffraction and powder neutron diffraction data.

phase has been calculated from the refinement at around 94% of phase volume fraction, with an estimated content of the previously mentioned bismuth oxycarbonate and copper oxide impurities of about 1% and 5% in weight, respectively. The crystallographic information file is provided in Supplementary Data 1.

No structural transitions or decomposition processes were observed, both on heating and cooling, in the 10–870 K temperature range, indicating a good metastability of the compound (Supplementary Fig. 5).

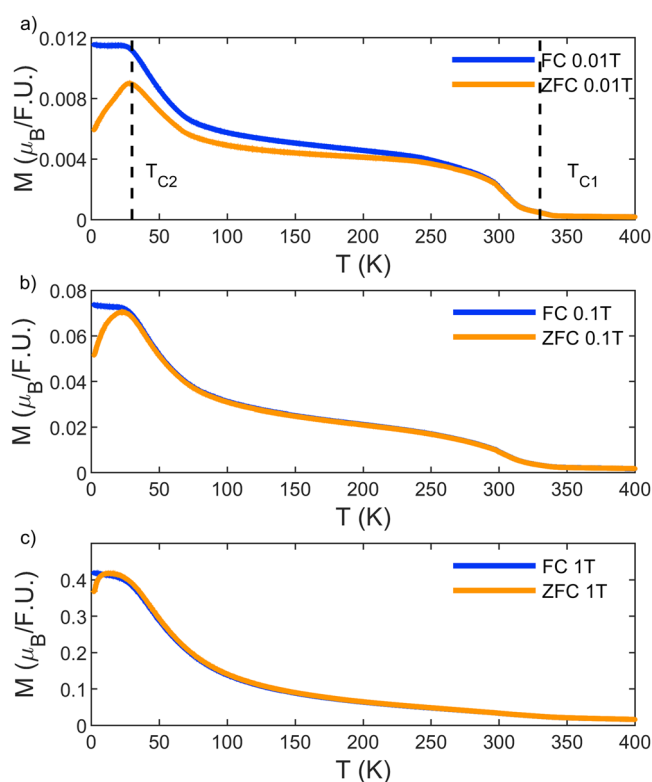
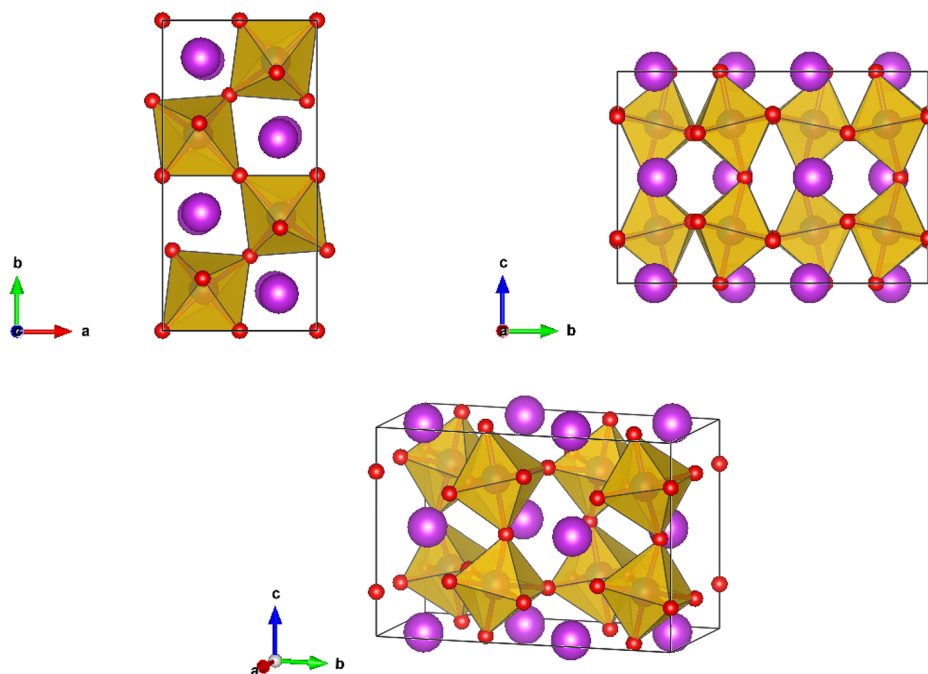
Magnetization

In Fig. 5, the DC SQUID zero field cooled (ZFC) and field cooled (FC) magnetization vs. temperature curves are shown for applied fields of 100 Oe

(a), 1000 Oe (b), and 10,000 Oe (c). Two magnetic transitions are visible in the explored thermal range, which varies their relative intensity with the magnitude of the applied magnetic field. At high temperatures (HT) the system sharply switches from the paramagnetic state to an ordered magnetic state with an onset temperature of about $T_{\text{C1}} = 330$ K (Fig. 5a), which is completely overlapped in the ZFC and FC measurements for all the explored external fields, suggesting the FM-like nature of such transition. The susceptibility trend $\chi^{-1}(T)$ at different magnetic fields (Supplementary Fig. 6) underlines a softening of the downturn at high H , compatible with the presence of a Griffiths phase^{55–58}, in which no long-range ordered FM clusters appear in a paramagnetic phase. The cluster nature of such phase is coherent with the observed two-step nature of this FM-like transition,

Fig. 4 | Unit cell of BiCu_{0.4}Mn_{0.6}O₃.

BiCu_{0.4}Mn_{0.6}O₃ unit cell projected along different crystallographic directions.

**Fig. 5 | Magnetization curves of BiCu_{0.4}Mn_{0.6}O₃ as a function of temperature.**

Zero field cooling (orange) and field cooling (blue) magnetization curves of BiCu_{0.4}Mn_{0.6}O₃ as a function of temperature measured at 100 Oe (a), 1000 Oe (b), and 10000 Oe (c). The thermal threshold for the ferromagnetic-like ($T_{C1} = 330$ K) and antiferromagnetic states ($T_{C2} = 30$ K) are marked with dashed black lines in (a).

clearly visible in Supplementary Fig. 6, probably arising from two phases that slightly differ in their Mn or Cu composition. The presence of clusters has been already reported in similar perovskite systems, such as in BiFe_{0.5}Mn_{0.5}O₃, in which inhomogeneities in the concentration of the Mn

and Fe ions (i.e., the formation of Fe- and Mn-rich clusters) significantly affect the magnetic properties^{24–26}. As the temperature is decreased, the compound undergoes a stabilization of the magnetic resultant below 250 K. At lower temperatures (LT), below 100 K, the magnetization starts to increase again with different trends for the ZFC and FC curves, displaying around $T_N = T_{C2} = 30$ K the feature of an AFM cusp in ZFC mode, which is flattened during the FC protocol. The absence of a flat saturation of the FM-like state magnetization below 250 K becomes more evident whether the external field is increased. In this thermal regime, a slight and gradual increase of the magnetization is clearly visible till the AFM order arises, suggesting the coexistence of two distinct magnetic populations. Specifically, a minor magnetic population leads to the formation of the FM-like state at HT, while a second predominant one, in its paramagnetic state for $T > T_{C2}$, only contributes to the AFM order. This observation supports an inhomogeneous and cluster-like distribution at the B site between Mn and Cu peculiar to Griffiths phases.

Some interesting features are: (1) the HT FM-like state involves a minority part of the material with respect to the AFM one, and it displays soft character (Figs. 5c and 6, blue curve); (2) crossing the T_{C1} order transition on cooling (FC) with a small field (0.01 T), the total magnetization of the HT-FM-like component increases compared to the ZFC (Fig. 5a). Vice versa, for larger fields ($H \geq 0.1$ T), ZFC and FC get superimposed in the range $T_{C2} < T < T_{C1}$, demonstrating that the saturation is reached also in ZFC conditions and thus suggesting the high polarizability of the HT-FM-like population (Fig. 5b, c) (3) a strong reduction of the separation between ZFC and FC below the AFM transition $T < T_{C2}$ as a function of the external field intensity, affecting also the shape of the ZFC with an almost complete quench of the cusp (Fig. 5). This may indicate that the AFM order has not a long-range character and it is confined at the mesoscale.

Magnetization versus field $M(H)$ measurements have been carried out at specific temperatures to analyze the magnetic regimes identified in BCMO by the previously reported $M(T)$ curves, as reported in Fig. 6. The paramagnetic state was confirmed by the linear trend of the $M(H)$ curve recorded at 370 K. As the system is brought down below T_{C1} , an FM-like loop is detected with negligible hysteresis down to T_{C2} . Moreover, the presence of a linear increasing trend of the curve in both negative and positive high field regimes confirms the presence of a superimposed paramagnetic population which becomes predominant when FM contribution saturates. From linear fitting of this trend, we extrapolate a saturation

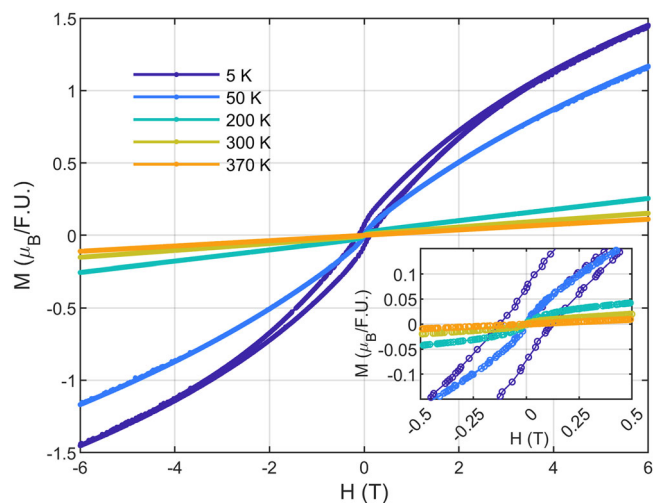


Fig. 6 | Magnetization curves of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ as a function of the external magnetic field. Magnetization vs. applied magnetic field measurement acquired in zero field cooling mode at different temperatures. Inset: zoom of the data at low field.

magnetization of $0.02 \mu_B$ per F.U. (Supplementary Fig. 7). It is worth noting that the rapid increase of the slope in the low field branches once the temperature is decreased progressively to 300 K, then 200 K down to 50 K (as highlighted by the $M(H)$ shape in the inset of Fig. 6) does not determine the formation of coercivity and remnant magnetization, demonstrating the very soft nature of FM state.

Just below T_{C2} , the hysteresis loop opens with a constricted shape across the zero-field regime, where a coercive field appears with $H_c \sim 1200$ Oe, thermally related to the stabilization of the AFM order observed in Fig. 5. The presence of such complexity in this LT loop reinforces the hypothesis of a superposition of two different magnetic populations or, at least, a magnetically disordered and inhomogeneous system, while the non-saturated loop marks the predominance of the AFM components with respect to the HT FM-like components in the high field regime. Moreover, the detection of a considerable number of Bohr magnetons below T_{C2} , over $1 \mu_B$ in the regime in which the branches of the loop are superimposed, suggests that a large part of the sample at 5 K is involved in magnetic interactions and AFM and FM subpopulations seem to be superimposed, as evidenced also by the opening of the hysteresis and the presence of remanent magnetization of about $0.08 \mu_B$ per F.U.

Temperature-dependent analysis of nuclear and magnetic structure

PND data has been collected in a large temperature range to assess the possibility of magnetic long-range ordering in the different thermal regions observed in the macroscopic characterizations. By cooling across T_{C1} no new magnetic peaks arise, nor we observed any changes in the intensity of the nuclear reflections at long d-spacing. These observations seem to point to the lack of long-range magnetic ordering across the T_{C1} critical temperature, typical of Griffiths phases, or that the order moment is below the resolution of the instrument. The lack of magnetic Bragg peaks can also be interpreted as being related to a spin glass state or a magnetically ordered state with a short correlation length, both cases can be consistent with the presence of an inhomogeneous distribution of the B site cations.

On cooling below T_{C2} , a weak broad peak arises at a d-spacing of $\sim 7.9 \text{ \AA}$ as highlighted in the inset of Fig. 7. Unfortunately, this is the only extra peak clearly observed below this temperature, and this can be related to the broad profile of the reflections coupled with the small sample mass and form factor contributions. The presence of just one magnetic reflection suggests that the long-range AFM state is characterized either by a small magnetic moment or that not all the sample contributes to this phase transition. Even if a single magnetic peak has been observed, and hence a solution of the magnetic

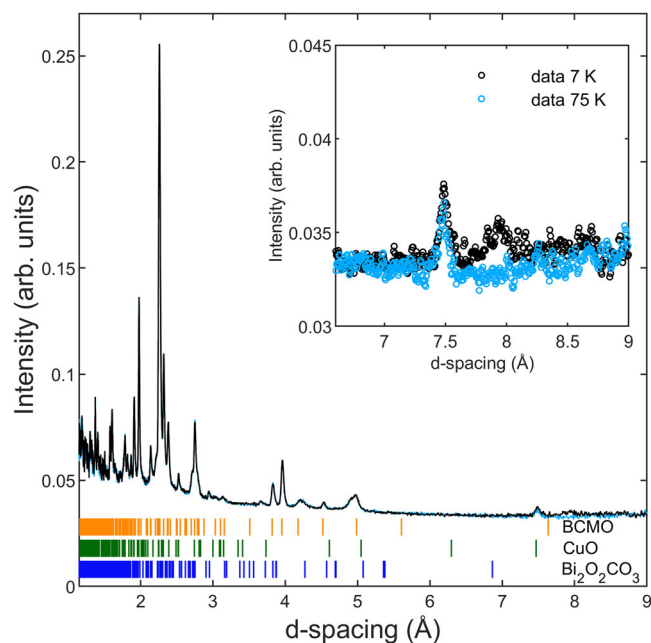


Fig. 7 | Neutron diffraction of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$. Neutron powder diffraction data of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ acquired at 7 K (black dots) and 75 K (light blue dots) on the WISH detector bank with an average 2θ of 58.3° . Expected reflections for $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ (orange tick marks), $\text{Bi}_2\text{O}_2\text{CO}_3$ (blue tick marks, ICSD cod. 202767), and CuO (green tick marks, ICSD cod. 16025) are shown. For CuO, both magnetic and nuclear reflections are reported in green. Inset: A weak magnetic peak arises at low temperatures at around $7.9 \text{ \AA}$, visible by comparing the 75 K and 7 K datasets.

structure is not possible, it has been investigated if this reflection was consistent with propagation vectors belonging to the special points of the $Pnma$ Brillouin zone. From this analysis, the only possible way to index this reflection is by considering the propagation vector $\mathbf{k} = (0.5, 0, 0)$. This, of course, does not exclude the possibility of an incommensurate propagation vector but the indexation which such propagation vector is not possible with a single reflection.

Nuclear magnetic resonance

Hyperfine-field ^{55}Mn NMR signals were detected from 1.4 K up to 260 K, an interval upper-limited by exceedingly short T_2 relaxation times above that temperature. Spin echoes were excited and detected in zero field (ZF) with a sizable rf enhancement $\eta \approx 1000$ typical of domain walls in a soft ferromagnet⁵⁹. Representative ZF ^{55}Mn spectra are shown in Fig. 8a. At $T > 50 \text{ K}$ they consist in a broad single asymmetric peak with a low-frequency shoulder, more evident at $T > 100 \text{ K}$, like that observed in the ^{55}Mn NMR spectra of double-exchange lanthanum manganites⁶⁰. Despite the large enhancement, the intensity of this signal is relatively weak, indicating that only a minority fraction of ^{55}Mn nuclei participate in this resonance. The mean frequency $\nu_L(T)$ of this resonance peak (Fig. 8b, blue bullets) apparently follows a regular order parameter curve extrapolating to zero at approximately 300 K, in fair agreement with T_{C1} determined by magnetization measurements, and approaches $\nu_L(0) \approx 330 \text{ MHz}$ (31.5 T in field units) at low temperature. The latter corresponds to an on-site atomic moment of $\approx 3 \mu_B$ at manganese^{60,61} and hence demonstrates a 4+ oxidation state for this Mn fraction, which is referred to henceforth as $\text{Mn}^{4+}(\text{I})$. The normalized $\text{Mn}^{4+}(\text{I})$ peak amplitude, proportional to the number of resonating nuclei (Fig. 8c, main panel), is constant on cooling down to 100 K, but it decreases to a minimum (discussed below) at approximately 30 K and recovers to the high-temperature value only at very low temperature.

On cooling below $T_{C2} \approx 35 \text{ K}$, further spectral components appear: a narrower peak at a frequency of $\approx 305 \text{ MHz}$ (Fig. 8b), in the range of Mn^{4+} too

Fig. 8 | Local magnetic components of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$. Zero Field ^{55}Mn nuclear magnetic resonance (NMR) spectra of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ at a few representative temperatures. The NMR peaks ascribable to $\text{Mn}^{4+}(\text{I})$, $\text{Mn}^{4+}(\text{II})$, and Mn^{3+} are highlighted in blue, pink, and green, respectively (a). Thermal evolution of Mn^{4+} NMR frequency (b). Normalized amplitude of the recorded NMR peaks as a function of temperature for $\text{Mn}^{4+}(\text{I})$ (main panel); and for $\text{Mn}^{4+}(\text{II})$ and Mn^{3+} (inset) (c).

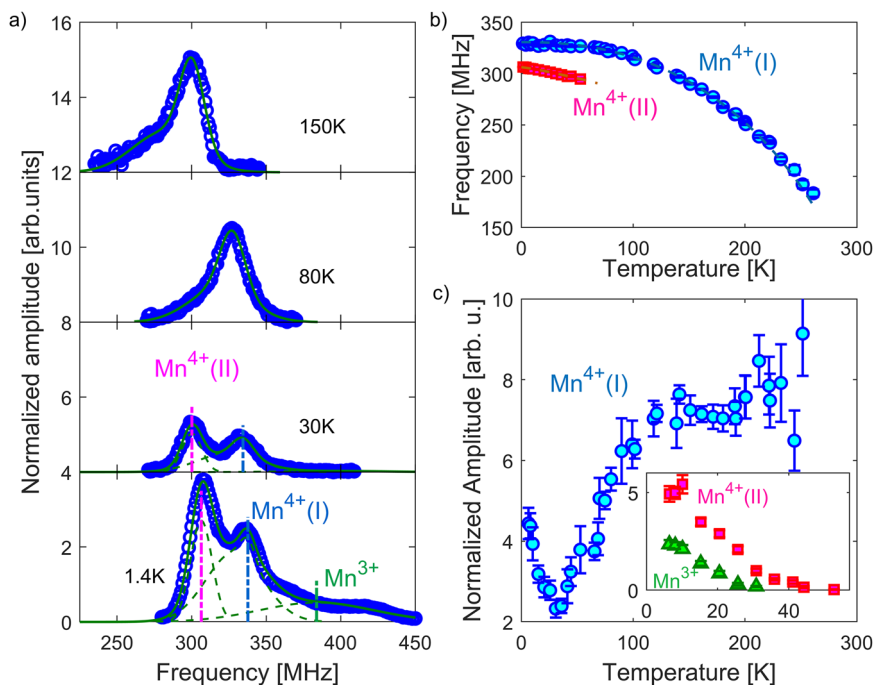
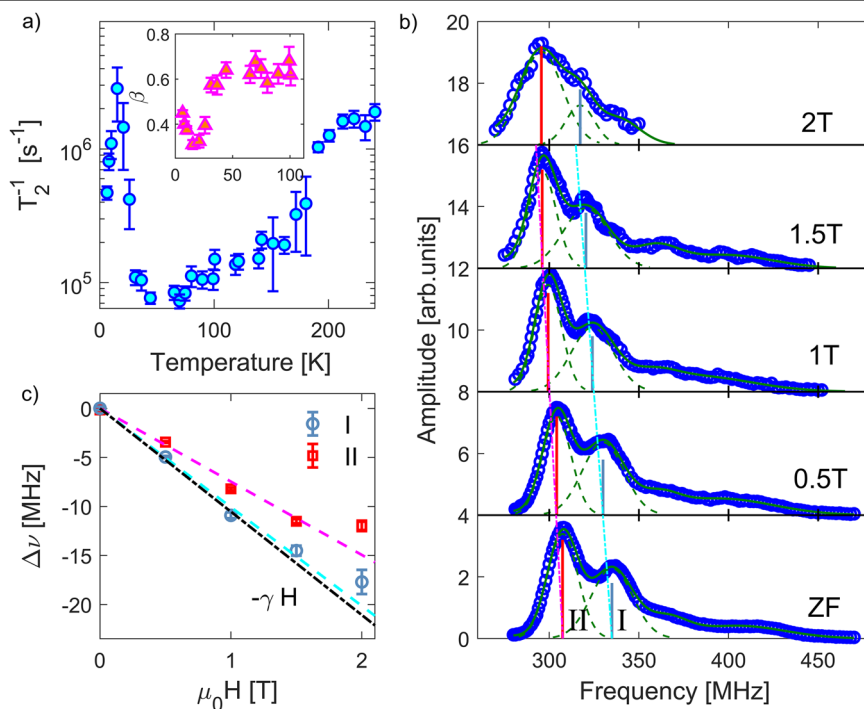


Fig. 9 | Local magnetic character of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$. Nuclear relaxation rate T_2^{-1} vs. temperature of $\text{Mn}^{4+}(\text{I})$; inset: stretching exponent β vs. T (a). Nuclear magnetic resonance spectra of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ in different applied magnetic fields at 1.4 K (b). Field dependence of the $\text{Mn}^{4+}(\text{I})$ and $\text{Mn}^{4+}(\text{II})$ resonance peaks (blue and red symbols, respectively) and best linear fits (dashed lines); the dash-dotted black line marks the expected behavior for a perfect collinear ferromagnetic arrangement (c).



(whence it is labeled here $\text{Mn}^{4+}(\text{II})$) and, at a slightly lower threshold temperature, a very broad shoulder spanning the 300–450 MHz frequency range appropriate for Mn^{3+} (ref. 62) (Fig. 8a). The huge linewidth of the latter stems from the anisotropic character of the open-shell Mn^{3+} ion, contrary to Mn^{4+} , leading to a very broad hyperfine field distribution due to its pseudo-dipolar anisotropic hyperfine term. The normalized amplitudes of these two components increase on cooling (inset of Fig. 8c) and, overall, approach a low-temperature value slightly larger than the amplitude of $\text{Mn}^{4+}(\text{I})$. This fact indicates that these signals arise from the independent magnetic ordering of additional Mn fractions, rather than from conversion of the $\text{Mn}^{4+}(\text{I})$ fraction.

Insight into the nature of the magnetic ordering of Mn^{3+} and $\text{Mn}^{4+}(\text{II})$ is provided by spin-spin nuclear relaxations rates T_2^{-1} of $\text{Mn}^{4+}(\text{I})$ over the whole temperature interval (Fig. 9a). Above 80 K, the latter follow the typical dependence of magnetic materials, namely, an increase with increasing temperature owing to the increase in the population of spin excitations (e.g. spin waves). Below 50 K, however, T_2^{-1} shows a steep upturn with a decreasing temperature and a sharp peak at $T_p \approx 20$ K. The latter is accompanied by stretched relaxation forms with stretching exponents $\beta \ll 1/2$, indicative of strong spatial inhomogeneities (Fig. 9a, inset). The T_2^{-1} peak temperature fairly agrees with the temperature at which the $\text{Mn}^{4+}(\text{I})$ signal amplitude exhibits a minimum, as pointed out above. The $\text{Mn}^{4+}(\text{I})$ signal

loss has the same origin, namely, exceedingly fast and inhomogeneous transverse relaxations, so that signal components with a relaxation time T_2 much shorter than the receiver dead time ($\approx 2 \mu\text{s}$) are not detected. The occurrence of a relaxation peak within a magnetically ordered phase typically denotes the slowing down of a diffusion dynamic of spin or, more likely, excitations, down to a complete freezing well below T_p , as previously reported for related compounds like low-doped manganites and layered cobaltates^{63,64}, and as also suggested by transport measurements in this compound (see below). Notably, the T_2^{-1} maximum and the related signal wipeout of $\text{Mn}^{4+}(\text{I})$ nearly coincide with the appearance of ordered Mn^{3+} and $\text{Mn}^{4+}(\text{II})$ fractions. This, on one hand, proves the existence of proximity coupling between the latter and the $\text{Mn}^{4+}(\text{I})$ fraction, as in the case of inter-dispersed phases, and rules out a trivial impurity phase for the minority $\text{Mn}^{4+}(\text{I})$ signal. On the other hand, this suggests that the magnetic transition detected by SQUID magnetometry at T_{C2} is triggered by charge freezing and the localization of static Mn^{3+} ions.

The magnetic order inside the $\text{Mn}^{4+}(\text{I})$ and $\text{Mn}^{4+}(\text{II})$ fractions was assessed by the application of moderate magnetic fields large enough to saturate the local moment, serving as a perturbation of the larger hyperfine field (the huge width of the Mn^{3+} spectrum does not warrant a reliable study). Spectra at 1.4 K shifts to a lower frequency with the applied field (Fig. 9b) due to its vector composition with the negative hyperfine field (i.e., opposite to the spin) of Mn ions. The two lines, however, exhibit different shift rates (Fig. 9c). The $\text{Mn}^{4+}(\text{I})$ line shifts with a slope $\mu_0^{-1} dv/dH \approx -\gamma/2\pi = -10.5 \text{ MHz T}^{-1}$ practically coincident with the gyromagnetic ratio of ^{55}Mn , as in the case of parallel alignment of electronic spins along the external field, i.e. in a collinear FM spin arrangement. The $\text{Mn}^{4+}(\text{II})$ line, on the other hand, though showing similar rf enhancement as the other one and hence exhibiting an FM character too, shifts with a fractional slope of $\approx -7.5 \text{ MHz T}^{-1}$, corresponding to an angle $\theta \approx 45^\circ$ between the spins and the external field, i.e. a canted spin arrangement with a canting angle $90^\circ - \theta$ relative to the ideal AFM structure. The large canting of this spin fraction, which seemingly contrasts the finding of a dominant AFM character below T_{C2} by SQUID magnetometry, can be reconciled if we notice that the amplitude of this signal is comparable to that of $\text{Mn}^{4+}(\text{I})$, while the SQUID response below T_{C2} in high fields overwhelms the weak FM magnetization at $T_{C2} < T < T_{C1}$. It is clear, therefore, that these $\text{Mn}^{4+}(\text{II})$ and Mn^{3+} signals do not represent the totality of spins undergoing magnetic order at T_{C2} but, plausibly, just the fraction at the interface with $\text{Mn}^{4+}(\text{I})$ clusters, as it is also indicated by the proximity effects in nuclear relaxations discussed above. This may explain why this spin fraction, though non-collinear, exhibits a more marked FM character than the missing majority spin fraction, which hasn't been detected in these NMR experiments.

Electrical transport characterization

The electrical transport of BCMO has been investigated, and the resistivity vs. temperature, measured in planar-plate configuration, is reported in Fig. 10. The system displays a semiconductive-like character with a conductive RT-state characterized by a resistivity of $10^3 \Omega\text{-cm}$, which rapidly evolves vs. T up to $3 \cdot 10^7 \Omega\text{-cm}$ at around 150 K. Below 140 K the resistivity of BCMO is no longer measurable and the material is probably in a dielectric state. Two distinct electrical regimes are present. At high temperatures, the resistivity curve follows the thermally activated (TA) trend expected for an ideal semiconductor. A fitting of these data with the Arrhenius model allows the estimation of an activation energy $E_A = (0.25 \pm 0.01) \text{ eV}$, confirmed by a good coefficient of determination of $R^2 = 0.9997$. Although the low resistivity values measured above 300 K appear noisy due to the low current applied during the measurement, the TA model describes well the electrical transport of BCMO above 190 K. On the contrary, a deviation from the Arrhenius linear plot is clearly visible below 190 K (inset Fig. 10a), a thermal regime where the high-temperature FM-like order completely stabilizes. By comparing the relative R^2 values, it has been proven that in this thermal range the resistivity behavior is more properly described by a 3D Mott's Variable Range Hopping model, as reported in the inset b of Fig. 10, with $R^2 = 0.9992$ (slightly higher than the values related to the other models at

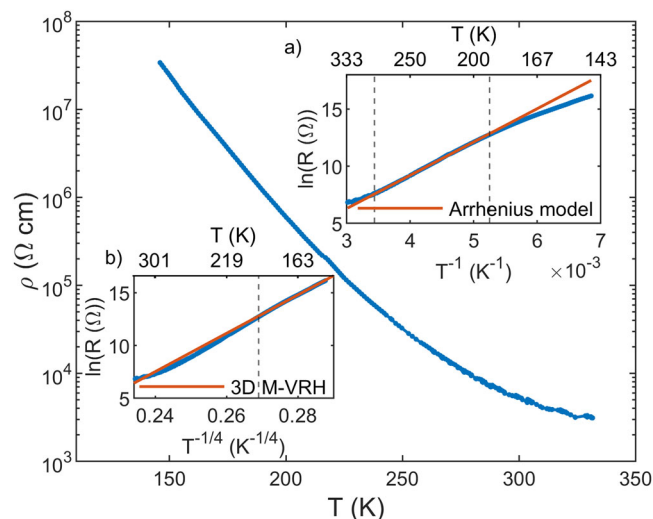


Fig. 10 | Electrical transport of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$. Resistivity vs. temperature of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ with high (HT) and low (LT) temperature ranges modeled in insets. The HT dataset is analyzed with the Arrhenius model (fit in the upper inset a), while the LT dataset better follows the 3D-Mott's Variable Range Hopping mechanism (fit in the lower inset b). The dashed black lines define the temperature limits where the fit has been carried out (HT from 300 K to 190 K (a), while LT from 190 K to 145 K (b)).

$R^2 = 0.9976$ and reported in Supplementary Fig. 8 and Supplementary Table 2), common electric transport mechanism in perovskites, especially when cationic disorder occurs⁶⁵. This result supports the hypothesis of different electronic transport paths along the three directions driven by Mott's variable range hopping mechanism, which can be driven by a partial localization of electrons on the transition metal B sites.

Discussion

The results reported on BCMO show the strong thermal-dependent interplay between its structural, magnetic, and electrical properties. $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$, characterized by Cu^{2+} deficiency, displays cationic disorder at the B-site and compositional inhomogeneities with the possible presence of localized regions at different manganese/copper concentrations. The charge neutrality of the compound is guaranteed by the presence of a partial Mn^{3+} population, verified by hyperfine-field NMR and XPS. The structural disorder and inhomogeneities lead to the absence of long-range magnetic ordering, as verified with PND experiments. However, although no structural modifications have been observed as a function of temperature from 7 to 870 K, the overall magnetism of BCMO shows, from SQUID and NMR measurements, a temperature-dependent evolution that correlates with its electrical transport properties.

BCMO shows different magnetic regimes at different temperatures:

(1) for $T > T_{C1} = 330 \text{ K}$, the system is paramagnetic, with a bad-conductive behavior characterized by resistivity values around $10^3 \Omega\text{-cm}$ and a thermally activated transport mechanism defined by an activation energy E_A around 0.26 eV.

(2) for $250 \text{ K} < T < T_{C1}$, the system undergoes an FM-like transition observed by SQUID magnetometry and NMR, where an FM population of $\text{Mn}^{4+}(\text{I})$ is detected as a very weak NMR signal. The comparison between the two techniques suggests that the FM-like onset arises from clusters with a fully FM order on a local scale driven by $\text{Mn}^{4+}\text{-Mn}^{4+}$ interactions (probably mediated by Cu^{2+}) with very soft character, and a small volume ($\approx 1\%$). Despite the occurrence of such an ordering process, the thermal-activated electronic transport observed at high temperatures persists in this temperature interval.

(3) for $70 \text{ K} < T < 250 \text{ K}$, while the FM-like state is completely saturated and the AFM is not established, a modification of the electronic transport regime is observed, better described by a variable range hopping mechanism

of the carriers. This is possibly ascribable to the partial localization of electrons at the manganese site, associated with the appearance, below T_{C2} , of a second magnetic population of Mn^{4+} (II) and Mn^{3+} detected by NMR in a distorted local FM order.

(4) lowering temperature in the range of 5–70 K yields a slight increase in the intensity of the overall magnetization, due to a major magnetic population with the formation of a typical AFM cusp trend with $T_{C2} = 30$ K. Neutron diffraction indicates the presence of long-range ordering (either with a very small ordered moment or with a small magnetic phase fraction) with a likely propagation vector $\mathbf{k} = (0.5, 0, 0)$. This magnetic phenomenology is strongly coupled with the observed increase of the resistivity, driven by the freezing of electrons which were responsible for the electrical transport at HT and now are localized on the Mn cations involved in the AFM order. This electron localization is confirmed by the arising of NMR resonance of Mn^{3+} . Coherently, a superposition of competitive magnetic responses, highlighted by the distorted shape of the magnetic hysteresis loops recorded at 5 K, confirms the coexistence of at least two magnetic ordered states (i.e. clusters FM and AFM) whose spatial segregation can be possibly ascribed to the structural inhomogeneities and disorder in the B-site distribution of Cu and Mn.

The nature of the magnetic clusters responsible for the overall weak FM moment below T_{C1} deserves a comment. Though spatially segregated from the majority magnetic phase of the material, we can safely rule out their coexistence in a trivial phase admixture. NMR spin-spin relaxations of ^{55}Mn provide stringent evidence that such FM clusters are coupled to the bulk of the material, which is only possible if they are small and finely inter-dispersed. The T_2^{-1} relaxations peak and the wipeout of the Mn^{4+} (I) signal over a broad temperature interval, which is closely related (Figs. 8c and 9a), coherently point to the slowing down of a diffusion dynamic of spin or charge excitations. However, the fact that such a diffusion process manifests itself over a temperature interval unrelated to T_{C1} and it is not accompanied by anomalies in the magnetic order parameter of Mn^{4+} (I), clearly points to charge fluctuations, which relax the nuclear spins via the nuclear quadrupole moment of ^{55}Mn . Notably, a charge diffusion regime is also witnessed by electric conductivity, fitting into a variable hopping range model over the same temperature interval, so that the two phenomena are strictly related one to another. However, electronic transport is a macroscopic probe of the whole sample volume and not of just a minute volume fraction. In summary, the FM clusters, though a minority, probe a diffusion process that affects the bulk of the material. This is only possible if they belong to the same structural phase of the majority fraction, and they are finely dispersed therein. Therefore, these FM clusters, though likely correlated to local deviations from the nominal stoichiometry unavoidable in a solid solution, may be viewed, in a sense, as an intrinsic property of this material.

Conclusions

$\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ (BCMO) has been synthesized under high pressure/high temperature (HP/HT) conditions and stabilized at ambient room conditions in a polycrystalline bulk form. This perovskite crystallizes in an orthorhombic system described by the centrosymmetric Pbam space group due to the stereochemical effect of the Bi^{3+} cations at the A site. The cation disorder at the B site and likely the presence of clusters with different concentrations of Cu^{2+} and $\text{Mn}^{4+}/\text{Mn}^{3+}$ species, leads to the absence of long-range magnetic order. Although no structural transitions have been detected from 7 K to 870 K, the overall magnetism of BCMO shows a temperature-dependent evolution which correlates with different electrical transport behaviors.

At HT, the system is paramagnetic, with a thermally activated electronic transport mechanism, while at $T_{C1} = 330$ K, BCMO undergoes an FM-like transition, probably driven by Mn^{4+} - Mn^{4+} interactions whose ordering is very soft and confined at the local scale. The thermal-activated transport is retained with the same characteristics up to the saturation of the FM order at around 250 K. At lower temperatures, a partial localization of the electrons on the manganese site, confirmed by the arising of the Mn^{3+} population, switches the electronic transport mechanism to a 3D variable

range hopping model, likely related to the cation disorder. At $T_{C2} = 30$ K the arising of an AFM order is observed compatible with a propagation vector $\mathbf{k} = (0.5, 0, 0)$. This magnetic behavior is coupled with a significant increase of the resistivity, guided by the freezing of electrons which were responsible for the electrical transport at HT and now are confined on the cations involved in the AFM order.

Despite the lack of a ferroelectric character, here excluded by crystal symmetry constraints, the FM-like state at HT of BCMO opens new perspectives for further studies on the solid solution $\text{BiCu}_{1-x}\text{Mn}_x\text{O}_3$ members and their possibly tuneable multifunctional states.

Methods

The synthesis of a polycrystalline sample of $\text{BiCu}_{0.4}\text{Mn}_{0.6}\text{O}_3$ (BCMO) has been carried out in a Walker-type multi anvil press by solid state reaction. Bi_2O_3 (99.999 %, Alfa Aesar Puratronic), CuO (99.99 %, Fluka), and MnO_2 (99.9 %, Alfa Aesar) have been mixed following the stoichiometry ratio 2:1:1 and ground in an agate mortar. The resulting powder has been packed in a thin, cold-welded Pt foil capsule. After the pressure reached the target value, the temperature was increased at a rate of $50^\circ\text{C min}^{-1}$, kept stable for the required reaction time, and then quenched to RT. The sample was finally slowly brought back to ambient pressure.

The morphology and chemical composition of BCMO were investigated by scanning electron microscopy (SEM) using a Zeiss Auriga Compact field-emission SEM, equipped with an Oxford Xplore 30 Energy Dispersive Spectroscopy (EDS) system.

Electron diffraction was performed with a Philips TECNAI F20 Transmission Electron Microscope (TEM/STEM) operating at 200 kV, equipped with an energy-dispersive X-ray spectrometer (EDXS). The STEM images were recorded using a high-angle annular dark field (HAADF) detector. The sample was ground in an agate mortar, suspended in isopropyl alcohol, and then sonicated for 3 h. A few drops of the solution were deposited on a gold grid coated with an amorphous carbon film. The powder has been investigated with selected area electron diffraction (SAED), high-resolution electron microscopy (HREM), and energy dispersive X-ray (EDS) analyses.

X-ray powder diffraction (PXRD) patterns were collected in Bragg-Brentano geometry on a Rigaku Smartlab XE diffractometer using Cu K_α wavelength ($\lambda = 1.5406 \text{ \AA}$). A Ni filter was used to suppress the K_β contribution. 5.0° Soller slits were used both on the incident and diffracted beam, and data were collected using a HyPix3000 detector. Measurements were performed in the 10 – 150° 2θ range with 0.01° step size, $0.5^\circ \text{ min}^{-1}$ speed, acquiring in continuous in 1D mode. Rietveld refinements were performed using the Jana2020 software⁴⁸.

Time of Flight (TOF) powder neutron diffraction (PND) experiments were carried out on the WISH instrument at the ISIS neutron and muon source, Didcot, UK⁶⁶. The diffraction data were collected at different temperatures (370 K, 300 K, 200 K, 75 K, and 7 K), counting for 3 h on a powdered sample of 103 mg, using a thin vanadium can as a sample holder. Neutron data are available in ref. 67.

Magnetic measurements were performed with a Quantum Design MPMS 3 SQUID magnetometer in the 2–400 K temperature range on a small fragment of the sample pellet ($m = 36.87(5) \text{ mg}$). The sample holder was a plastic straw, and the pellet was kept in a gelatine capsule and fixed using Teflon tape. DC zero-field cooling (ZFC), field cooling (FC), and field cooling-warming (FCW) measurements were performed at selected applied field in the range 0.001–1 T. Magnetization versus field measurements were performed with the same sample set up at different temperatures in the applied field range ± 6 T. Additional measurements have been carried out on a Quantum Design MPMS-XL 5 T SQUID magnetometer.

A Keithley 2182A nanovoltmeter and a Keithley 2400 source meter were utilized for the Electrical transport measurements. The measured sample was an as-synthesized pellet disk (with a radius of around 2 mm, thinned down to a thickness of around 0.3 mm), double-side polished to reduce the surface roughness below a few μm . The resistivity was calculated by Ohm's law in the two-contact configuration, with platinum contacts

(thickness ~100 nm) sputtered on both faces of a planar-plate disk, and evaluated in the thermal range between 140 K and 340 K. A current of about 20 μ A have been applied.

⁵⁵Mn Nuclear Magnetic Resonance (NMR) experiments, both in zero fields (ZF) mode or by applying a perturbative external magnetic field (up to 2 T), were performed by means of a home-built phase-coherent spectrometer, the 'HyReSpect', also varying the temperature thanks to a heater for HT and helium or nitrogen flow. Powdered samples of about 20 mg were placed in an untuned probe head consisting of a small coil, as described in ref. 68. The spectra were recorded point by point by exciting spin echoes at discrete frequencies by means of a standard P- τ -P pulse sequence. The digitized echo signals were analyzed by the fast Fourier transform (FFT).

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific ESCALAB QXi spectrometer employing a monochromatic Al K α X-ray source (1486.6 eV) with a spot size of 650 μ m $\times$ 200 μ m circa. Charge compensation was applied, and magnetic lenses were switched off. High-resolution spectra were recorded using a constant pass energy (20 eV), at 0.1 eV step⁻¹, with a dwell time of 50 ms. For further experimental details, refer to ref. 69.

Data availability

Data available on request from the corresponding author. The raw files of the neutron diffraction data collected on the WISH diffractometer can be found at <https://doi.org/10.5286/ISIS.E.RB2320119>, whereas the input file for the JANA2020 refinement of the room temperature neutron and X-ray data are embedded in the cif file provided as supporting information.

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Author contributions

C.C. and D.D. synthesized the bulk samples. C.C. and F.M. carried out the X-ray diffraction experiments and performed data analysis. C.C. and F.O. performed the neutron diffraction experiments and analyzed the data. C.C., D.D., and F.C. performed the SQUID measurements; D.D. interpreted the magnetometric data, and M.S. participated in the analysis. A.M. performed

transmission electron microscopy and analyzed the data. G.T. performed scanning electron microscopy. G.A. collected and interpreted the nuclear magnetic resonance data. R.C. collected and analyzed resistivity data. M.R. and L.A. performed and analyzed the X-ray photoelectron spectroscopy measurements. C.C., D.D., F.O., and E.G. discussed the results. D.D. and E.G. supervised the research. All the authors contributed to the manuscript; writing was supervised by C.C. and D.D.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Chiara Coppi.

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