

Pressure-induced multiple structural phase transitions on multiferroic $\text{CaMn}_7\text{O}_{12}$

W.C. Ferreira^{a,*}, A. Nonato^b, J. Mira^c, M. Sánchez-Andujar^d, M.A. Senãris-Rodríguez^d, S. Yañez-Vilar^c, A.P. Ayala^e, C.W.A. Paschoal^e

^a Lyman Laboratory of Physics, Harvard University, Cambridge, MA, 02138, USA

^b Curso Ciências Naturais, Universidade Federal do Maranhão, Campos, 65700-000, Bacabal, MA, Brazil

^c Departamento de Física Aplicada and Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, 15782, Santiago de Compostela, Spain

^d Universidade da Coruña, QUIMOLMAT Group, Dpt. Chemistry, Faculty of Science and Centro Interdisciplinar de Química e Bioloxía (CICA), Zapateira, 15071, A Coruña, Spain

^e Departamento de Física, Universidade Federal do Ceará, Campus do Pici, 65455-900, Fortaleza, CE, Brazil

ARTICLE INFO

Keywords:

$\text{CaMn}_7\text{O}_{12}$

Phase transitions

Synchrotron radiation

X-ray diffraction

Multiferroic

ABSTRACT

$\text{CaMn}_7\text{O}_{12}$ (CMO) is an outstanding multiferroic material known for its significant magnetically-induced electric polarization. Its strong magnetoelectric (ME) effect, i.e., electric polarization controlled via magnetic fields or vice versa, makes this material suitable for a variety of technological applications. In this study, we employed synchrotron X-ray powder diffraction to explore polycrystalline CMO's pressure-induced structural phase transitions (SPTs). Our results indicate that CMO undergoes two distinct pressure-induced SPTs: the first transition occurs at pressures above 7.0 GPa, changing from a rhombohedral to an orthorhombic structure, and the second occurs around 13.0 GPa, transforming into a monoclinic structure. These findings differ from the pressure-induced behavior of CMO single crystals and highlight CMO as one of the rare quadruple perovskites exhibiting multiple pressure-induced non-isostructural phase transitions. This study expands the understanding of phase stability behavior in multiferroic materials under high-pressure conditions.

1. Introduction

$\text{CaMn}_7\text{O}_{12}$ (CMO), an A-site-ordered quadruple perovskite family member, has attracted significant attention due to its exceptional multiferroic properties, particularly its record-setting magnetically-induced electric polarization [1–4]. The origin of magnetically induced polarization in CMO has been extensively debated in the literature and remains controversial [5–9]. Currently, to explain the origin of the giant electric polarization in CMO, two distinct models have been proposed: the first one argues that magneto-orbital ordering is a prerequisite for stabilizing the chiral magnetic structure of CMO [10], and the giant electric polarization is induced by symmetric exchange striction, which determines the polarization magnitude, and the Dzyaloshinskii-Moriya (DM) interaction, driving the polarization direction [7,10,11]. However, very recently, it was shown that the giant spin-induced electric polarization in CMO is allowed even in the absence of orbital ordering [6], which contradicts the hypothesis proposed by Perks N et al. [10]. Although these models have been widely employed to explain the

magnetically-induced ferroelectricity observed in other quadruple perovskites like $\text{SrMn}_7\text{O}_{12}$, $\text{PbMn}_7\text{O}_{12}$, and $\text{CdMn}_7\text{O}_{12}$ [12], based on pyroelectric and bias electric field measurement, Tereda et al. suggested that such high electric polarization in quadruple perovskites is not intrinsic but due to thermally stimulated currents (TSC) [13].

CMO undergoes an unusual phase transition at low temperatures, exhibiting an unconventional incommensurate orbital ordering at 250 K [2,14,15]. Two antiferromagnetic (AFM) transitions were recorded at $T_{N1} = 90$ K and $T_{N2} = 45$ K, associated with a long-range helical AFM order and a second magnetic transition that modifies the helical magnetic state [8,9,16], respectively, but no additional structural phase transitions were observed below 250 K. Despite the extensive studies on CMO's ferroelectric and magnetic properties [3,6,9], few studies have focused on its structural phase transition (SPT). Przenioslo et al. found that at high temperatures, around 400 K, CMO undergoes a SPT from the Rhombohedral phase, space group $R\bar{3}$, to a cubic phase, space group $Im\bar{3}$ with both phases coexisting until temperatures of around 440 K [17]. Above 440 K, the structure becomes solely cubic. CMO's observed

* Corresponding author.

E-mail address: wcastroferreira@fas.harvard.edu (W.C. Ferreira).

<https://doi.org/10.1016/j.physb.2024.416603>

Received 22 June 2024; Received in revised form 13 August 2024; Accepted 5 October 2024

Available online 5 October 2024

0921-4526/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

temperature-dependent phase transition is characterized by simultaneous structural changes and charge-ordering [17–20].

Recently, a high-pressure investigation showed that the isostructural quadruple perovskite $\text{NaMn}_7\text{O}_{12}$ exhibits an insulator-to-semimetal transition around 18 GPa. Such transition is due to Mn charge transfer, which leads to a metallic behavior [21]. High pressure does not affect the $\text{NaMn}_7\text{O}_{12}$ crystalline structure. Regarding CMO, the effect of the Sr-substitution, which generates a "negative" chemical pressure in the structure since the Sr ion is bigger than Ca, was investigated [22]. In this case, the authors observed a decrease in the $R\bar{3} \rightarrow Im\bar{3}$ structural phase transition temperature, but no change in the electric properties was observed. These results suggested that high pressures could induce structural changes in CMO.

Stekiel et al. recently reported a pressure-induced SPT on CMO single crystals [23]. The same structural phase transition is found at high temperatures [17]. In contrast with the high-temperature phase transition, the authors have not observed any sign of reflection splitting characteristic of the $R\bar{3} \rightarrow Im\bar{3}$ phase transition. Instead, they observed changes in the Mn-O distances leading to the regularization of MnO_6 octahedra. This regularization suggests an increase in symmetry, which led the authors to conclude that the high-temperature CMO SPT takes place at 28 GPa. In this paper, we investigate the structural behavior of polycrystalline CMO under high hydrostatic pressure conditions. Our results show that polycrystalline CMO undergoes two pressure-induced structural phase transitions for the pressure range studied in this paper.

2. Experimental

Polycrystalline CMO powder was prepared at room temperature by the Pechini method as described elsewhere [14]. For this purpose, stoichiometric amounts of CaCO_3 (Panreac, >98 %) and $\text{Mn}(\text{NO}_3)_2\text{H}_2\text{O}$ (Aldrich, >98 %) were dissolved in a 1M citric acid aqueous solution and then added the same volume of ethylene glycol. After, the obtained solution was diluted in 100 ml of water. The resulting solution was then heated at 200 °C until a highly viscous resin was formed, whose organic matter was decomposed at 400 °C, obtaining the precursor powder. The precursor powder was placed in an agate mortar and carefully ground for about 20 min with a pestle until a homogenous black powder was obtained. The powder was heated in air at 800 °C/60 h, 900 °C/24 h (two times), and 950 °C/24 h (two times), respectively, with intermediate grinding and pelletizing. Synchrotron X-ray Powder Diffraction (SXRPD) experiments were performed at the XDS beamline of the Brazilian Synchrotron Laboratory (LNLS) under high-pressure conditions using monochromatic synchrotron radiation with $\lambda = 0.602495$ Å. More details about this beamline can be found in Ref. [24]. High pressure was applied using a diamond anvil cell (DAC) with Ne gas as pressure-transmitting media for hydrostatic conditions. Small ruby chips were loaded together with the sample in the gasket to determine the pressure values by measuring its luminescence emission. The patterns were collected at pressures up to 18.9 GPa. After closing the DAC, the initial pressure was 3.0 GPa. The experiments were performed in the range from 3.0 GPa up to 18.9 GPa. The two-dimensional SXRPD patterns were integrated to provide intensity as a function of 2θ using the software FIT2D [25]. Le Bail method [26] was employed to obtain structural information using FullProf software [27] with initial lattice parameters obtained from the room pressure phase data [28]. The peak of Mn_3O_4 hausmannite secondary phase, common in CMO synthesis [29, 30], was not considered in the fit. For the diffractograms where the ambient pressure structure does not reproduce the measured data, the Dicvol06 [31] algorithm, available in WinPLOTR [32], was used to index the new phases. The higher figure of merit (FoM) [33] was used to check the reliability of the solutions, and the lattice parameters obtained from Dicvol06 were used as a starting point to perform the Le Bail method.

3. Results and discussions

Fig. 1 shows the pressure-dependent SXRPD patterns obtained for CMO. Additional peaks at $2\theta = 12.6^\circ$ and 14.0° indicate a small amount (less than 2 %) of Mn_3O_4 (hausmannite). It is worth noting that trace amounts of manganese oxide are frequently found in this compost, regardless of the synthesis method [4,34,35]. The broad diffraction peak around $2\theta = 17.2^\circ$ is due to the steel gasket [36]. Also, we observe a ruby peak around $2\theta = 15.6^\circ$. At lower pressures, the known $R\bar{3}$ rhombohedral phase fits well with the SXRPD pattern, and CMO powder patterns can be described by the $R\bar{3}$ phase up to 7.0 GPa. However, upon this pressure value, remarkable changes in the crystalline structure evidenced by the emergence of new peaks suggest the existence of a pressure-induced phase transition (see Fig. 2), e.g., notice the splitting of the peak at 19.2° . The splitting is observed weakly at 8.0 GPa, as highlighted in Fig. 2b. Similarly, at 13.3 GPa, further changes in the SXRPD pattern are observed, such as a new peak at $2\theta \cong 17.0^\circ$. Above this pressure value, no remarkable changes in diffraction patterns were noted up to 18.9 GPa, indicating that CMO does not undergo any other SPT up to the maximum pressure investigated in this work.

First, we checked if these transformations could be a decomposition since CMO can be decomposed into CaMn_3O_6 and Mn_2O_3 under pressure changes. At high pressures, cubic Mn_2O_3 transforms into an orthorhombic structure [29]. However, considering the synchrotron radiation used in our experiments ($\lambda = 0.602495$ Å), all pressure-dependent diffraction patterns investigated by Hong et al. [29] should exhibit a strong peak at $2\theta = 12.8^\circ$, which is not observed in our diffraction patterns. Besides, the structural phase transition observed for Mn_2O_3 by synchrotron X-ray diffraction is for pressures above 18.5 GPa. Unfortunately, investigations on CaMn_3O_6 were not reported under pressure.

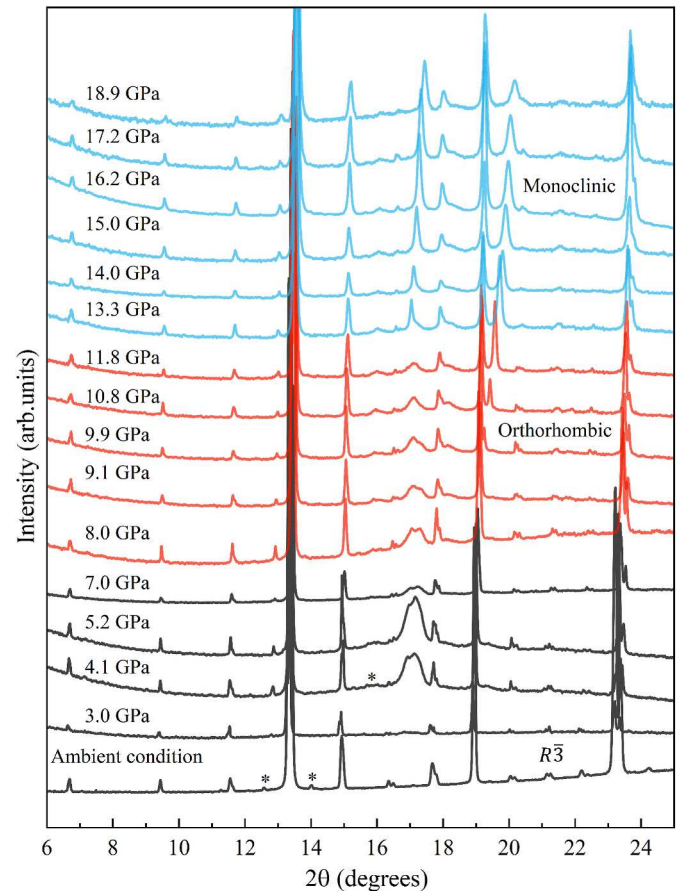


Fig. 1. Pressure-dependent SXRPD diffractograms obtained for $\text{CaMn}_7\text{O}_{12}$. The asterisk symbol (*) marks minor traces of Mn_3O_4 hausmannite and ruby peaks.

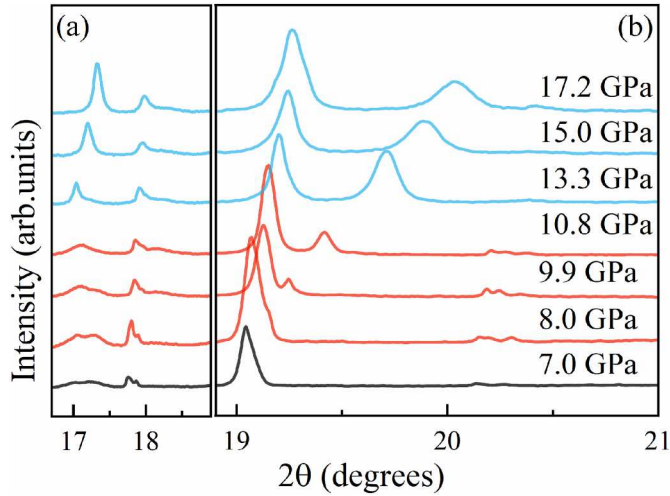


Fig. 2. Selected diffractograms highlighting the pressure-induced changes on the $\text{CaMn}_7\text{O}_{12}$ compound.

At room pressure, Hadermann et al. [30] reported that CaMn_3O_6 crystallizes into a monoclinic structure belonging to the $P2_1/a$ space group. As in Mn_2O_3 , we compared CMO and CaMn_3O_6 diffraction patterns for pressure up to 18.9 GPa. The analysis revealed that no diffraction peaks exhibited by CMO coincide with CaMn_3O_6 . If we suppose that CaMn_3O_6 does not undergo any phase transformations at high pressure, a diffraction peak shift due to the volume contraction is expected. However, even with this shift, the diffraction patterns do not coincide. So, we can assume that the transformation observed into CMO under pressure is not a decomposition into CaMn_3O_6 and Mn_2O_3 , instead of a structural phase transition (SPT).

Due to the limited angular range imposed by the diamond anvil cell, it was impossible to perform a complete structural resolution. Instead, a detailed investigation using the Le Bail method was applied to check the adequate symmetry of high-pressure patterns. The low-pressure patterns were successfully indexed with a rhombohedral structure (Fig. 3). Above 7.0 GPa, the new diffraction peaks do not satisfy the primary extinction rule of the rhombohedral phase ($-h + k + l = 3n$, n is an integer), and this crystalline system can no longer describe the crystal lattice.

The high-pressure patterns above 7.0 GPa were indexed as an orthorhombic system using the Dicvol06 program based on the best FoM [25]. The splitting of the rhombohedral (042) peak at $2\theta \cong 19.2^\circ$ into the (002) and (151) orthorhombic reflections at $2\theta \cong 19.2^\circ$ and 19.4° , respectively, defines the onset of the first pressure-induced structural phase transition undergone by CMO. Hence, the rhombohedral lattice parameters turn into an orthorhombic with $a_o \cong \sqrt{3}a_{\text{rh}}$, $b_o \cong a_{\text{rh}}$, $c_o \cong 1/2c_{\text{rh}}$. To have insights into the best high-pressure crystal symmetry of CMO, we performed a search for a pseudosymmetry of the monoclinic lattice using the Bilbao Crystallographic Server platform tools. The search suggests a C-centered orthorhombic system in the 8.0 GPa–11.8 GPa pressure range. The orthorhombic proposed high-pressure system (space group $Cmmm$) of $\text{CaMn}_7\text{O}_{12}$ at 8.0 GPa has the following lattice parameters: $a = 15.3293$ (17) Å, $b = 10.2744$ (10) Å, $c = 3.6245$ (6) Å and $V = 570.86$ (13). The pressure dependence of lattice parameters is shown in Fig. 4a. The change in lattice parameters shows a reduction in the stacking along [001] direction.

The proposed orthorhombic model adjusts the patterns up to 11.8 GPa; however, above this pressure value, the Le Bail fit did not provide reliable results, and a satisfactory orthorhombic model was not achieved. For pressures higher than 11.8 GPa, the CMO compound experiences a new structural phase transition from an orthorhombic to a monoclinic system (space group $C2/m$), with lattice parameters close to the orthorhombic one with a monoclinic angle $\beta = 94.4$ (3)° and $a = 15.3260$ (27) Å, $b = 10.2108$ (82) Å, $c = 3.6188$ (2) Å, $V = 546.68$ (56)

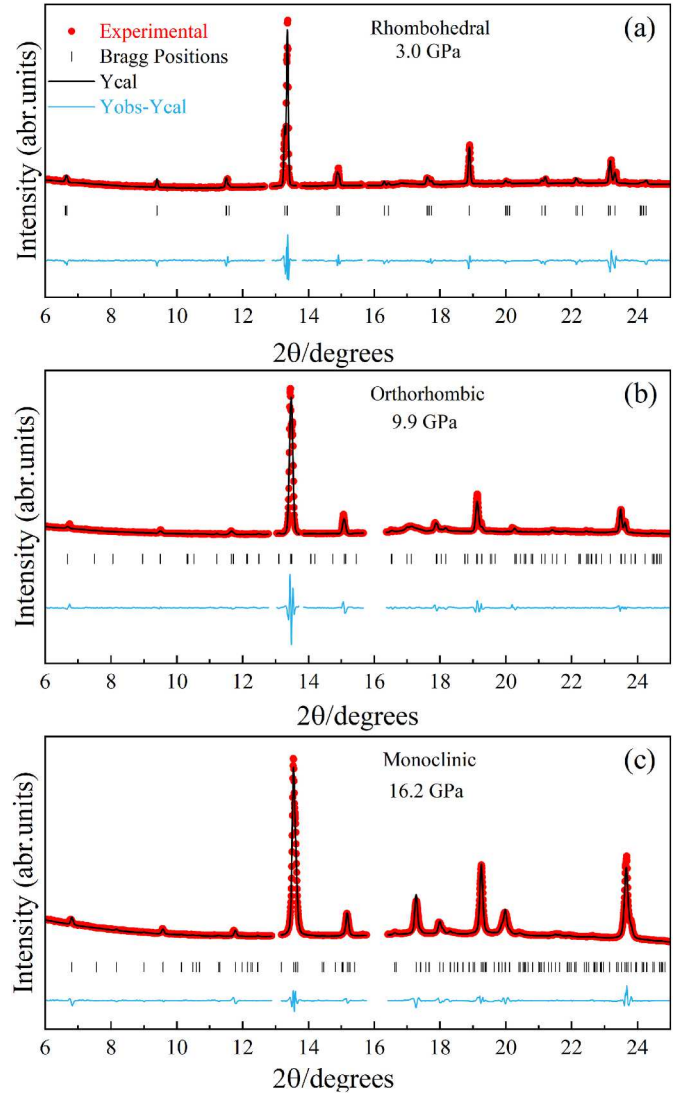


Fig. 3. Le Bail fitting of SXRPD pattern of CMO at (a) 3.0 GPa, (b) 9.9 GPa, and (c) 16.2 GPa. The breaks correspond to the Mn_3O_4 hausmannite secondary phase, and ruby peaks are excluded from the fits.

(See Fig. 4a–c). This new SPT undergone by CMO could be strongly related to the high overlapping of the broad peaks and the appearance of a new reflection (510) at $2\theta \cong 17.0^\circ$, which is highlighted in Fig. 2a. The Le Bail fit considered the W parameter of the Caglioti's relationship for the FWHM peak profile. This parameter can monitor the peak's broadness and may be sensitive to structural phase transitions [32]. As shown in Fig. 4b, the W parameter pressure dependence clearly shows change trends in good agreement with the onset of the structural phase transitions experienced by CMO.

In Fig. 4c, it is evident that the unit cell volume increases when there is a phase transition from the orthorhombic to the monoclinic structure. This increase in volume can be attributed to a negative pressure effect on the CMO. It is not unexpected, as negative chemical pressure on the CMO structure was observed due to the Sr-substitution [22]. Moreover, it has been reported that the CMO displays a negative thermal expansion coefficient at high temperatures for the cubic phase [37]. Similar negative pressure effects have been noted in other perovskite structures, demonstrating how this occurrence can significantly impact these materials' structural, electronic, and magnetic properties [38–40].

Unfortunately, the number of diffraction peaks hindered the determination of the crystalline structure. Thus, just the crystalline system in each phase was identified. However, we can investigate the bulk

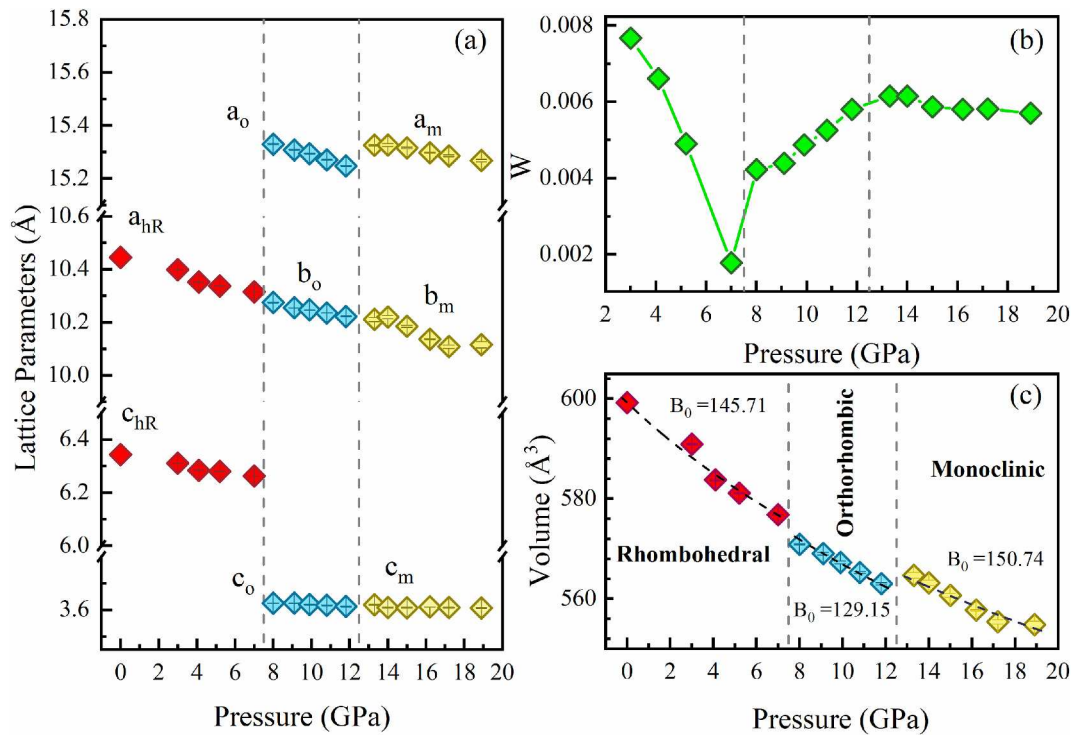


Fig. 4. Pressure-dependent crystalline structural data for CMO. Grey vertical dashed lines indicated the proposal phase transitions. (a) Lattice parameters. (b) The FWHM (W) of CMO. (c) Pressure-dependent volume. Dashed black lines indicate the best fit by the Birch-Murnaghan equation.

modulus from the volume curves. The Bulk modulus can be obtained from the Birch–Murnaghan equation of state [41,42].

$$P(V) = \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right\} \quad (1)$$

where P is the pressure, V_0 is the reference volume, V is the deformed volume, B_0 is the bulk modulus and B'_0 is the bulk modulus derivative with relation to the pressure. The Birch–Murnaghan (BM) fit is shown in Fig. 4c. The dashed black line in Fig. 4 shows the best BM fit for the pressure-dependent volume of CMO. The volume decreasing due to the pressure increase is almost linear (linear fits with $R^2 > 0.95$), which suggests an elastic constant (derivative of the bulk modulus) approximately equal to 4. Assuming this value in both phases, which is a usual procedure in linear behaviors in similar materials (see Ref. [43]), the best fit in the rhombohedral phase shows that the bulk modulus is 145.7 GPa. The bulk modulus for the orthorhombic and monoclinic phases is 129.1 GPa and 150.7 GPa, respectively. These values are compatible with those observed in $\text{LaMn}_7\text{O}_{12}$ by Bhadram et al. [43]

As discussed before, $\text{NaMn}_7\text{O}_{12}$ was submitted to high hydrostatic pressure up to 40 GPa, but no SPT was observed. The crystalline structure of this compound was investigated using single-crystal X-ray diffraction, whereas electrical resistance measurements carried out on powdered samples showed an insulator-to-semimetal transformation in the electric behavior. Also, $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ exhibits an isostructural phase transition at 3.5 GPa [44], in which a first-order charge-transfer transition from a $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$ low-pressure phase to a high-pressure $\text{LaCu}_3^{2+}\text{Fe}_4^{3.75+}\text{O}_{12}$ was observed. In both cases, $\text{NaMn}_7\text{O}_{12}$ and $\text{LaCu}_3\text{Fe}_4\text{O}_{12}$, a volume reduction was found at the electric transitions. Finally, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was investigated up to 46 GPa by synchrotron X-ray powder diffraction, and any SPT was observed [45]. Recently, Bhadram et al. [43] reported a structural phase transition in the monoclinic ($I2/m$) $\text{LaMn}_7\text{O}_{12}$ (LMO) quadruple perovskite to a cubic $Im\bar{3}$ symmetry at 34 GPa, which is the same phase for high-temperature conditions. Both compounds, CMO and LMO, have the same $Im\bar{3}$ symmetry at high temperatures. CMO and LMO are the first quadruple perovskites where

pressure-induced non-isostructural phase transitions were observed. The high-pressure phase for polycrystalline CMO is not the same as the high temperature experienced by LMO. Instead, CMO experiences two symmetry-lowering phase transitions under high-pressure conditions. To our knowledge, the first quadruple perovskite exhibits multiple pressure-induced structural phase transitions.

It is particularly interesting to note that the pressure-induced phase transitions on the polycrystalline $\text{CaMn}_7\text{O}_{12}$ (CMO) sample marked by the splitting of the rhombohedral (042) peak at $2\theta \cong 19.2^\circ$ and with the appearance of new peaks differ from that reported for $\text{CaMn}_7\text{O}_{12}$ single crystals [23]. Some works reported ionic substitution in $\text{CaMn}_7\text{O}_{12}$ may induce a rhombohedral-cubic phase transition at room temperature [35, 46,47]. A reduction of the unit cell in these systems usually accompanies such phase transition. Additionally, have been reported that at high temperatures, the CMO exhibits a negative thermal expansion coefficient for the cubic phase [37]. This suggests that it is possible a pressure-induced rhombohedral-cubic phase transition in CMO for pressures higher than 20 GPa.

4. Conclusions

Our study demonstrated that polycrystalline $\text{CaMn}_7\text{O}_{12}$ (CMO) undergoes two significant pressure-induced structural phase transitions. Initially, at pressures above 7.0 GPa, the rhombohedral structure transitions to an orthorhombic phase, followed by a subsequent transition to a monoclinic phase at 13.0 GPa. Both phase transitions in polycrystalline CMO imply symmetry lowering, which is the first observation in quadruple perovskite. These findings enhance our understanding of its stability behavior under high hydrostatic pressure conditions, expanding the potential of CMO and similar quadruple perovskites in applications where pressure-induced phase transitions could be advantageous.

CRedit authorship contribution statement

W.C. Ferreira: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **A. Nonato:**

Writing – review & editing, Validation, Methodology, Investigation. **J. Mira:** Writing – review & editing, Validation. **M. Sánchez-Andujar:** Writing – review & editing, Validation. **M.A. Senarís-Rodríguez:** Writing – review & editing, Validation. **S. Yáñez-Vilar:** Writing – review & editing, Validation. **A.P. Ayala:** Writing – review & editing, Validation, Methodology, Funding acquisition. **C.W.A. Paschoal:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

Acknowledgements

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico —CNPq (Grants 310353/2023-8 and 406322/2022-8) for financial support. M.S.A and M.A.S.R acknowledge Grant PID2021-122532OB-I00 funded by MICIU/AEI/10.13039/501100011033 and by ERDF/EU. This research used the Brazilian Synchrotron Light Laboratory (LNLS) facilities, part of the Brazilian Center for Research in Energy and Materials (CNPEM). The XDS beam-line staff is acknowledged for their assistance during the experiments (Proposal 20160695).

References

- [1] S. Yáñez-Vilar, A. Castro-Couceiro, B. Rivas-Murias, A. Fondado, J. Mira, J. Rivas, M.A. Senarís-Rodríguez, High dielectric constant in the charge-ordered manganese oxide $\text{CaMn}_7\text{O}_{12}$, *Z. Anorg. Allg. Chem.* 631 (2005) 2192–2196, <https://doi.org/10.1002/zaac.200570040>.
- [2] J.T. Zhang, X.M. Lu, J. Zhou, H. Sun, F.Z. Huang, J.S. Zhu, Magnetic properties and origins of ferroelectric polarization in multiferroic $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* Condens. Matter 87 (2013) 1–6, <https://doi.org/10.1103/PhysRevB.87.075127>.
- [3] 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, <https://doi.org/10.1039/d1dt02992d>.
- [4] A. Castro-Couceiro, S. Yáñez-Vilar, B. Rivas-Murias, A. Fondado, J. Mira, J. Rivas, M.A. Senarís-Rodríguez, Dielectric properties of the charge-ordered mixed oxide $\text{CaMn}_7\text{O}_{12}$, *J. Phys. Condens. Matter* 18 (2006) 3803–3815, <https://doi.org/10.1088/0953-8984/18/15/023>.
- [5] A. Huon, A.M. Vibhakar, A.J. Grutter, J.A. Borchers, S. Disseler, Y. Liu, W. Tian, F. Orlandi, P. Manuel, D.D. Khalyavin, Y. Sharma, A. Herklotz, H.N. Lee, M. R. Fitzsimmons, R.D. Johnson, S.J. May, Helical magnetism in Sr-doped $\text{CaMn}_7\text{O}_{12}$ films, *Phys. Rev. B* 98 (2018), <https://doi.org/10.1103/PhysRevB.98.224419>.
- [6] D. Lu, J. Yang, J. Zhang, H. Zhao, M. Pi, X. Ye, X. Wang, Z. Pan, C. Dong, L. He, F. Shen, C.Y. Kuo, C. Te Chen, Z. Hu, P. Yu, Y. Shen, Y. Long, Giant spin-induced electric polarization in absence of orbital order in $(\text{Bi}_{0.5}\text{Ag}_{0.5})\text{Mn}_7\text{O}_{12}$, *Phys. Rev. B* 109 (2024), <https://doi.org/10.1103/PhysRevB.109.174417>.
- [7] X.Z. Lu, M.H. Whangbo, S. Dong, X.G. Gong, H.J. Xiang, Giant ferroelectric polarization of $\text{CaMn}_7\text{O}_{12}$ induced by a combined effect of Dzyaloshinskii-Moriya interaction and exchange striction, *Phys. Rev. Lett.* 108 (2012) 1–5, <https://doi.org/10.1103/PhysRevLett.108.187204>.
- [8] G. Zhang, S. Dong, Z. Yan, Y. Guo, Q. Zhang, S. Yunoki, E. Dagotto, J.-M. Liu, Multiferroic properties of $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* 84 (2011) 174413, <https://doi.org/10.1103/PhysRevB.84.174413>.
- [9] R.D. Johnson, L.C. Chapon, D.D. Khalyavin, P. Manuel, P.G. Radaelli, C. Martin, Giant improper ferroelectricity in the ferroaxial magnet $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. Lett.* 108 (2012) 2–5, <https://doi.org/10.1103/PhysRevLett.108.067201>.
- [10] N.J. Perks, R.D. Johnson, C. Martin, L.C. Chapon, P.G. Radaelli, Magneto-orbital helices as a route to coupling magnetism and ferroelectricity in multiferroic $\text{CaMn}_7\text{O}_{12}$, *Nat. Commun.* 3 (2012) 1276–1277, <https://doi.org/10.1038/ncomms2294>.
- [11] K. Cao, R.D. Johnson, N. Perks, F. Giustino, P.G. Radaelli, First-principles study of structurally modulated multiferroic $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* Condens. Matter 91 (2015) 1–6, <https://doi.org/10.1103/PhysRevB.91.064422>.
- [12] Y.S. Glazkova, N. Terada, Y. Matsushita, Y. Katsuya, M. Tanaka, A.V. Sobolev, I. A. Presniakov, A.A. Belik, High-pressure synthesis, crystal structures, and properties of $\text{CdMn}_7\text{O}_{12}$ and $\text{SrMn}_7\text{O}_{12}$ perovskites, *Inorg. Chem.* 54 (2015) 9081–9091, <https://doi.org/10.1021/acs.inorgchem.5b01472>.
- [13] N. Terada, Y.S. Glazkova, A.A. Belik, Differentiation between ferroelectricity and thermally stimulated current in pyrocurrent measurements of multiferroic $\text{MMn}_7\text{O}_{12}$ (M = Ca, Sr, Cd, Pb), *Phys. Rev. B* 93 (2016) 12–17, <https://doi.org/10.1103/PhysRevB.93.155127>.
- [14] A. Nonato, B.S. Araujo, A.P. Ayala, A.P. Maciel, S. Yáñez-Vilar, M. Sanchez-Andujar, M.A. Senarís-Rodríguez, C.W.A. Paschoal, Spin-phonon and magnetostriiction phenomena in $\text{CaMn}_7\text{O}_{12}$ helimagnet probed by Raman spectroscopy, *Appl. Phys. Lett.* 105 (2014) 1–5, <https://doi.org/10.1063/1.4902234>.
- [15] S.M. Souliou, Y. Li, X. Du, M. Le Tacon, A. Bosak, Soft-phonon-driven orbital order in $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* 94 (2016) 1–6, <https://doi.org/10.1103/PhysRevB.94.184309>.
- [16] X. Du, R. Yuan, L. Duan, C. Wang, Y. Hu, Y. Li, Soft vibrational mode associated with incommensurate orbital order in multiferroic $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* Condens. Matter 90 (2014) 1–7, <https://doi.org/10.1103/PhysRevB.90.104414>.
- [17] R. Przenioslo, I. Sosnowska, E. Suard, A. Hewat, A.N. Fitch, Phase coexistence in the charge ordering transition in $\text{CaMn}_7\text{O}_{12}$, *J. Phys. Condens. Matter* 14 (2002) 5747–5753, <https://doi.org/10.1088/0953-8984/14/23/308>.
- [18] A.N. Vasil'ev, O.S. Volkova, New functional materials (Review), *Low Temp. Phys.* 11, v.33 (2007) 895–914, <https://doi.org/10.1063/1.2747047>.
- [19] M.N. Iliev, V.G. Hadjiev, M.M. Gospodinov, R.P. Nikolova, M.V. Abrashev, Raman study of phonons in $\text{CaMn}_7\text{O}_{12}$: effects of structural modulation and structural transition, *Phys. Rev. B* Condens. Matter 89 (2014) 1–6, <https://doi.org/10.1103/PhysRevB.89.214302>.
- [20] I.O. Troyanchuk, A.N. Chobot, Phase transition in $\text{CaMn}_3(\text{Mn}_3^{3+}\text{Mn}^{4+})\text{O}_{12}$ with the perovskite structure, *Crystallogr. Rep.* 42 (1997) 983–989, <https://doi.org/10.1134/1.170718>.
- [21] D. Delmonte, F. Mezzadri, F. Orlandi, G. Calestani, Y. Amiel, E. Giloli, High Pressure Induced Insulator-to-Semimetal Transition through Intersite Charge Transfer in $\text{NaMn}_7\text{O}_{12}$, *Crystals* 8 (2018) 81, <https://doi.org/10.3390/cryst8020081>.
- [22] A. Huon, D. Lee, A. Herklotz, M.R. Fitzsimmons, H.N. Lee, S.J. May, Effect of chemical pressure on the electronic phase transition in $\text{Ca}_{1-x}\text{Sr}_x\text{Mn}_7\text{O}_{12}$ films, *Appl. Mater.* 5 (2017) 096105, <https://doi.org/10.1063/1.4994089>.
- [23] M. Stekiel, A. Girard, D. Zimmer, V. Monteseuro, K. Glazyrin, I. de Pedro, L. Bayarjargal, B. Winkler, J. Ruiz-Fuertes, Pressure-induced charge ordering transition in $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* 105 (2022) 064110, <https://doi.org/10.1103/PhysRevB.105.064110>.
- [24] F.A. Lima, M.E. Saleta, R.J.S. Pagliuca, M.A. Eleotério, R.D. Reis, J.F. Júnior, B. Meyer, E.M. Bittar, N.M. Souza-Neto, E. Granado, XDS: a flexible beamline for X-ray diffraction and spectroscopy at the Brazilian synchrotron, *J. Synchrotron Radiat.* 23 (2016) 1538–1549, <https://doi.org/10.1107/S160057751601403X>.
- [25] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Hausermann, Two-dimensional detector software: from real detector to idealised image or two-theta scan, *High Pres. Res.* 14 (1996) 235–248, <https://doi.org/10.1080/08957959608201408>.
- [26] A. Le Bail, H. Duroy, J.L. Fourquet, Ab-initio structure determination of LiSbWO_6 by X-ray powder diffraction, *Mater. Res. Bull.* 23 (1988) 447–452, [https://doi.org/10.1016/0025-5408\(88\)90019-0](https://doi.org/10.1016/0025-5408(88)90019-0).
- [27] J. Rodríguez-Carvajal, Fullprof: a program for rietveld refinement and pattern matching analysis. Abstract of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, 1990, p. 127.
- [28] W. Ślawiński, R. Przenioslo, I. Sosnowska, M. Bieringer, Structural and magnetic modulations in $\text{CaCu}_x\text{Mn}_{7-x}\text{O}_{12}$, *J. Phys. Condens. Matter* 22 (2010) 186001, <https://doi.org/10.1088/0953-8984/22/18/186001>.
- [29] F. Hong, B. Yue, N. Hirao, Z. Liu, B. Chen, Significant improvement in Mn_2O_3 transition metal oxide electrical conductivity via high pressure, *Sci. Rep.* 7 (2017) 44078, <https://doi.org/10.1038/srep44078>.
- [30] J. Hadermann, A.M. Abakumov, L.J. Gillie, C. Martin, M. Hervieu, Coupled cation and charge ordering in the CaMn_3O_6 tunnel structure, *Chem. Mater.* 18 (2006) 5530–5536, <https://doi.org/10.1021/cm0618998>.
- [31] A. Boulfif, D. Louër, Powder pattern indexing with the dichotomy method, *J. Appl. Crystallogr.* 37 (2004) 724–731, <https://doi.org/10.1107/S0021889804014876>.
- [32] W.C. Ferreira, G.L.C. Rodrigues, B.S. Araújo, F.A.A. de Aguiar, A.N.A. de Abreu Silva, P.B.A. Fechine, C.W. de Araujo Paschoal, A.P. Ayala, Pressure-induced structural phase transitions in the multiferroic four-layer Aurivillius ceramic $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$, *Ceram. Int.* 46 (2020) 18056–18062, <https://doi.org/10.1016/j.ceramint.2020.04.122>.
- [33] P.M. de Wolff, A simplified criterion for the reliability of a powder pattern indexing, *J. Appl. Crystallogr.* 1 (1968) 108–113, <https://doi.org/10.1107/S002188986800508X>.
- [34] J. Sannigrahi, S. Chattopadhyay, D. Dutta, S. Giri, S. Majumdar, Magnetic and electric properties of $\text{CaMn}_7\text{O}_{12}$ based multiferroic compounds: effect of electron doping, *J. Phys. Condens. Matter* 25 (2013), <https://doi.org/10.1088/0953-8984/25/24/246001>.
- [35] A. Nonato, S. Yáñez-Vilar, M. Sánchez-Andujar, J. Mira, M.A. Senarís-Rodríguez, C.W.A. Paschoal, Impact of Co-doping on the structural and magnetic properties of multiferroic $\text{CaMn}_7\text{O}_{12}$, *J. Alloys Compd.* 740 (2018) 559–566, <https://doi.org/10.1016/j.jallcom.2017.11.260>.
- [36] D. He, Y. Zhao, T.D. Sheng, R.B. Schwarz, J. Qian, K.A. Lokshin, S. Bobev, L. Daemen, H.K. Mao, J.Z. Hu, J. Shu, J. Xu, Bulk metallic glass gasket for high pressure, in situ x-ray diffraction, *Rev. Sci. Instrum.* 74 (2003) 3012–3016, <https://doi.org/10.1063/1.1575926>.
- [37] K. Gautam, D.K. Shukla, S. Francoual, J. Bednarcik, J.R.L. Mardegan, H.-P. Liermann, R. Sankar, F.C. Chou, D.M. Phase, J. Stremper, Large negative

- thermal expansion in the cubic phase of $\text{CaMn}_7\text{O}_{12}$, *Phys. Rev. B* 95 (2017) 144112, <https://doi.org/10.1103/PhysRevB.95.144112>.
- [38] H. Sakai, S. Yokoyama, A. Kuwabara, J.S. White, E. Canévet, H.M. Rønnow, T. Koretsune, R. Arita, A. Miyake, M. Tokunaga, Y. Tokura, S. Ishiwata, Negative-pressure-induced helimagnetism in ferromagnetic cubic perovskites $\text{Sr}_{1-x}\text{Ba}_x\text{CoO}_3$, *Phys. Rev. Mater.* 2 (2018), <https://doi.org/10.1103/PhysRevMaterials.2.104412>.
- [39] X. Li, Y. Fu, L. Pedesseau, P. Guo, S. Cuthriell, I. Hadar, J. Even, C. Katan, C. C. Stoumpos, R.D. Schaller, E. Harel, M.G. Kanatzidis, Negative pressure engineering with large cage cations in 2D halide perovskites causes lattice softening, *J. Am. Chem. Soc.* 142 (2020) 11486–11496, <https://doi.org/10.1021/jacs.0c03860>.
- [40] A. Kvasov, L.J. McGilly, J. Wang, Z. Shi, C.S. Sandu, T. Sluka, A.K. Tagantsev, N. Setter, Piezoelectric enhancement under negative pressure, *Nat. Commun.* 7 (2016) 12136, <https://doi.org/10.1038/ncomms12136>.
- [41] F. Birch, Finite elastic strain of cubic crystals, *Phys. Rev.* 71 (1947) 809–824, <https://doi.org/10.1103/PhysRev.71.809>.
- [42] F.D. Murnaghan, The compressibility of media under extreme pressures, *Proc. Natl. Acad. Sci. USA* 30 (1944) 244–247, <https://doi.org/10.1073/pnas.30.9.244>.
- [43] V.S. Bhadram, B. Joseph, D. Delmonte, E. Gilioli, B. Baptiste, Y. Le Godec, R.P.S. M. Lobo, A. Gauzzi, Pressure-induced structural phase transition and suppression of Jahn-Teller distortion in the quadruple perovskite structure, *Phys. Rev. Mater.* 5 (2021) 104411, <https://doi.org/10.1103/PhysRevMaterials.5.104411>.
- [44] Y.W. Long, T. Kawakami, W.T. Chen, T. Saito, T. Watanuki, Y. Nakakura, Q.Q. Liu, C.Q. Jin, Y. Shimakawa, Pressure effect on intersite charge transfer in A-site-ordered double-perovskite-structure oxide, *Chem. Mater.* 24 (2012) 2235–2239, <https://doi.org/10.1021/cm301267e>.
- [45] D. Valim, A.G. Souza Filho, P.T.C. Freire, S.B. Fagan, A.P. Ayala, J. Mendes Filho, A.F.L. Almeida, P.B.A. Fechine, A.S.B. Sombra, J. Staun Olsen, L. Gerward, Raman scattering and x-ray diffraction studies of polycrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ under high-pressure, *Phys. Rev. B* 70 (2004) 132103, <https://doi.org/10.1103/PhysRevB.70.132103>.
- [46] Md Motin Seikh, V. Caignaert, O.I. Lebedev, B. Raveau, Cubic structure and canted antiferromagnetism of $\text{CaMn}_7\text{O}_{12}$ doped with trivalent cations (Fe, Al, Cr), *Solid State Commun.* 180 (2014) 52–55, <https://doi.org/10.1016/j.ssc.2013.11.024>.
- [47] W.-T. Chen, C.-W. Wang, C.-C. Cheng, Y.-C. Chuang, A. Simonov, N.C. Bristowe, M. S. Senn, Striping of orbital-order with charge-disorder in optimally doped manganites, *Nat. Commun.* 12 (2021) 6319, <https://doi.org/10.1038/s41467-021-26625-w>.