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Introduction

Multiferroic materials are promising candidates for next generation of multifunctional technological applications based on the dual control of magnetization/polarization by application of electric/magnetic fields.^{1,2} Among these materials are the strongly correlated electron systems (SCE) which can exhibit magnetoelectric (ME) effects through the coupling between spins and lattice by combining non-centrosymmetric structures and complex magnetic orders. Some of these special cases can be observed in manganite systems³ one representative example of which is the hexagonal LuMnO₃ which exhibits ferroelectricity (FE) coexisting

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Novel multiferroic state and ME enhancement by breaking the AFM frustration in $LuMn_{1-x}O_3$ †

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This study provides a comprehensive insight into the effects of controlled off-stoichiometry on the structural and multiferroic properties of the hexagonal manganite $LuMn_{1-x}O_{3+\delta}$ (x = 0.02; $\delta \sim 0$), supported by neutron powder diffraction measurements confirming single phase $P6_3cm$ symmetry and evidencing a relevant ferromagnetic component, below $T_N \sim 90$ K, which breaks the archetypal geometrically frustrated antiferromagnetic state typically ascribed to $LuMnO_3$. The perturbations in the triangular disposition of spins prompt an additional electric polarization contribution and a clear enhancement of the magnetoelectric coupling which are in good agreement with the results of first principles calculations. In addition, Raman spectroscopy, dielectric permittivity, pyroelectric current and magnetic measurements as a function of temperature point out the precursor effects of the magnetic phase transitions involving a strong coupling between spins, lattice and electric order, even above the Néel temperature.

with a geometrically frustrated canted antiferromagnetic (C-AFM) structure below $T_{\rm N} \sim 90$ K.⁴ The formal description of the LuMnO₃ structure is based on the arrangement of regular MnO5 bipyramid layers, where the dominant superexchange interaction occurs in basal planes, constraining spin orientations by an angle of 120° between the nearest neighbor (NN) Mn³⁺ ions, forming a regular triangular arrangement. Overall magnetic frustration is ensured by the interaction between next near neighbors (NNN) in the perpendicular axis, rendering opposite spin dispositions between adjacent planes, dictating an AFM order below $T_{\rm N} \sim 90 \text{ K.}^5$ In this scenario, the appearance of ionic vacancies of either O²⁻, Lu³⁺ or Mn³⁺ can lead to local perturbations in the orbital hybridization, corresponding to a redistribution of spatial charges with subsequent structural adjustments in adjacent Mn-O bond lengths and Mn-O-Mn angles,⁶ which alter the respective transfer integral of the conformed exchange interactions between neighboring Mn³⁺ ions. These changes in the balance between NN and NNN interactions were proposed to stabilize magnetic states of higher energy and promote a ferroelectric polarization component.⁵ Previous studies on the self-doped LuMn_{1-x}O_{3+ δ} (|x| < 0.1; $\delta \sim 0$) system confirmed that magnetic properties are changed while retaining the overall phase structural symmetry,⁷ hence demonstrating that it is possible to introduce charge redistributions and inhomogeneities in order to perturb the balance between the supercharge interactions and interfere with the triangular AFM frustration.⁸ The present study aims to further explore the possibility to promote local and subtle disturbances in the Mn³⁺ ions "sub-lattice", as

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found in the LuMnO₃, towards changes in the magnetic structure encompassing finite changes in the FE polarization, and consequently enhancing the intrinsic magnetoelectric coupling.^{9,10}

Experimental methods

The synthesis of polycrystalline samples, as well as essential composition and structural and magnetic characterization, is described in a previous work.⁷ A more detailed study is hereby carried out on the sample with deliberate off-stoichiometry LuMn_{0.98}O₃ which was confirmed to be free of contamination and spurious phases. Neutron powder diffraction (NPD) measurements were performed using the fine resolution powder diffractometer E9 at Helmholtz-Zentrum Berlin, Germany, with λ = 1.79821 Å and at fixed temperatures of 2, 10, 50, 80, 100 and 300 K. Additional measurements were performed using the Powgen (time-of-flight diffractometer, with 1 Å bandwidth) instrument at the Spallation Neutron Source at Oak Ridge National Laboratory, USA, with central $\lambda = 1.066$ Å and $\lambda = 2.665$ Å and at 10, 80 and 300 K. Structural Rietveld refinements were performed using FullProf software.¹¹ First-principles density functional theory (DFT) as implemented in the code VASP^{12,13} with the projector augmented wave method¹⁴ was used. The Perdew-Burke-Ernzerhof generalized gradient exchange-correlation approximation¹⁵ was applied considering PBE+*U*, with $U_{eff} = U - J = 8$ eV applied to the Mn d orbitals according to the Dudarev approach.¹⁶ The convergence of the electric polarization was checked with respect to the energy cutoff and number of k-points. The valence electrons considered for calculations for Lu are 5s²6s²5p⁶5d¹, for Mn 3p⁶3d⁶4s¹, and for O 2s²2p⁴. Non-polarized micro Raman spectroscopy was performed with a T64000 Jobin-Yvon spectrometer in a backscattering geometry and in the 150 to 900 cm^{-1} range, using the 514.5 nm line of an argon laser as the excitation source. The laser spot size was $\sim 1.5 \ \mu m$ and its impinging power was kept at 2 mW preventing sample heating. Measurements were performed in the temperature range from 10 to 350 K using a He closed cycle cryogenic system (Displex ADP-Cryostat HC-2), equipped with a silicon diode and a digital temperature controller (Scientific Instruments, model 9650) which enables sample temperature reading with a precision of 0.1 K. In order to perform electric measurements the sample was cut as a parallel plate (1 mm thick \times 18 mm^2 area) and gold electrodes were sputtered in the wider faces. The complex dielectric permittivity ($\varepsilon' + i\varepsilon''$) was measured using a HP4284A Precision LCR Meter under a driving signal of 1 V_{ac} and in the frequency range between 10^3 and 2×10^6 Hz. Pyroelectric current was measured using a Keithley 617 electrometer by recurring to a short-circuit method that enabled suppression of other sources of electric charge in the electrodes except that of pyroelectric origin. The measurements were also carried out under opposite electric fields up to 300 V_{dc} to ascertain that no internal field exists in the sample. Different heating rates from 4 to 7 K min⁻¹ were tested in order to optimize the signal-to-noise ratio while avoiding thermal inhomogeneity in the sample. Magnetization measurements used a Cryogenic Ltd VSM system and a Quantum Design MPMS SQUID.

Results and discussion

Fig. 1 shows the NPD pattern of the LuMn_{0.98}O₃ sample recorded at 10 K along with the simulated pattern obtained from the respective Rietveld refinement of the atomic positions, assuming the space group P63cm. The complete list of lattice parameters, atomic positions, magnetic moment vectors, and refinement quality factors is presented as ESI.[†] The temperature dependence of the lattice parameters, the Mn-O bond lengths and the Mn-O-Mn bond angle is presented in Fig. 2. The lattice parameters obtained at 300 K $(a, b = 6.0448 \text{ Å}; c = 11.3653 \text{ Å}; \text{ vol.} = 359.646 \text{ Å}^3)$ are in good agreement ($\Delta < 0.06\%$) with previous XRD results of the same sample $(a, b = 6.046 \text{ Å}; c = 11.366 \text{ Å}; \text{ vol.} = 359.82 \text{ Å}^3),^7$ both revealing a subtle increase of the unit cell volume ($\sim 0.2\%$) in comparison to compounds with strict stoichiometry (a, b = 6.04 ± 0.002 Å; $c = 11.36 \pm 0.001$ Å; vol. = 359.0 ± 0.03 Å³).^{4,7,17} Such an effect is mainly due to a slight increase of a and bparameters ($\sim 0.1\%$) rendered by stretching ($\sim 1\%$) of Mn–O bond lengths located in the basal plane. This suggests that the Wyckoff positions 2a, 4b and 6c can accommodate the Mn vacancies, with consequential anionic repulsion contributing to the perceived cell volume expansion. Overall temperature dependence of the Lu_{0.98}MnO₃ lattice parameters follows the same trends of the stoichiometric compound reported by S. Lee et al.4 Thermal expansion from 50 to 300 K is almost linear reaching $\sim 0.4\%$ and involving mainly *a*, *b* parameters while a slight contraction is observed in the *c* parameter. The phase transition between the magnetically ordered to the paramagnetic (PM) state cannot be perceived from the temperature dependence of a, b and c parameters; nevertheless it can be clearly noticed from the anomalies of the Mn-O-Mn bond angle and the Mn-O bond distance between 80 and 100 K. A minor lattice expansion occurs on cooling from 50 K to 10 K suggesting some structural rearrangements. The volume of the cell at 10 K (a, b = 6.030 Å; c = 11.367 Å; vol. = 357.96 Å³) is only ~0.1% larger than that of LuMnO₃ reference data ($a, b \sim 6.027$ Å;



Fig. 1 Rietveld difference plot of LuMn_{0.98}O₃ NPD data collected at 10 K.



 $c \sim 11.364$ Å; vol. ~ 357.60 Å³).^{4,6} Below 10 K a sudden $(\sim 0.1\%)$ contraction of the cell is observed converging to parameters similar to those of the stoichiometric compound⁴ as Mn-O3-Mn and Mn-O4-Mn bond angles become similar. Even though charge compensation mechanisms can theoretically lead up to 6% electrons default for a 2% Mn deficit, overall, no cell tightening is manifested, as could be likely from the occurrence of a smaller Mn4+-O bond. Nonetheless, in the hexagonal system the MnO₅ bipyramid arrangements are not prompt to the formation of Mn⁴⁺ ions as it can happen in the MnO₆ octahedron of the orthorhombic manganites.^{5,18} Charge balance can also be compensated by partial oxygen deficiency $(\delta \text{ up to } -0.003^7)$, which could justify the higher temperature required for sintering off-stoichiometric samples in comparison to the stoichiometric LuMnO₃, in order to achieve single phase quality and homogeneity.7

Fig. 3 presents a more detailed analysis of the NPD patterns obtained at different fixed temperatures in the 21 to $42^{\circ} 2\theta$ range. The indexation of the most prominent reflections marked as 101, 102, 103 and 201 is attributed to the antiferromagnetic order within basal planes and compatible with the $P6_3cm$ space group. The occurrence of a paramagnetic phase transition is attested by the disappearance of these peaks above



Fig. 3 Comparison of NPD obtained at 2, 10, 50, 80, 100 and 300 K, using P1 magnetic structure indexation.

 $T_{\rm N} \sim 90$ K. The presence of an additional diffraction peak at $2\theta \sim 39^{\circ}$ can be identified through emulating all possible reflections by recurring to the same lattice parameters and a lower $P\bar{1}$ symmetry group. This peak indexed as 112 shows a relative increase at lower temperatures and is not compatible with the symmetry rules of a strict antiferromagnetic order; hence it can be considered as a contribution of some ferromagnetic (FM) order. No noteworthy contributions from the antiferromagnetic structure could be observed for the 100 K NPD diagram, being generally similar to the 300 K measurement. In any case, the resolution for fitting complex magnetic configurations in the diffractograms is limited due to thermal effects.¹⁹ The refinement simulation process of the magnetic structure applies slight variations of the magnetic moment (μ_i) intensity for each of the six Mn³⁺ positions in the unit cell, without necessarily compromising the P6₃cm space group symmetry.¹⁰ In fact, the small asymmetries between distinct Mn-O3 and Mn-O4 basal bonds are estimated to fall below 8% and can correspond to minor variations of orbital hybridization and respective μ_i . None the less, for practical purposes we consider an average magnetic moment value $\langle \mu \rangle_{\rm Mn}$ for all Mn ions as calculated from Rietveld refinements. The most interesting result is a non-compensated magnetic moment calculated for the hexagonal unit cells below 90 K, having a finite summation over the 6 Mn³⁺ ions with projections $\Sigma \mu_x$, $\Sigma \mu_y$, $\Sigma \mu_z$ and overall $|\mu|_{\text{cell}} = (\Sigma \mu_x^2 + \Sigma \mu_y^2 + \Sigma \mu_z^2)^{1/2}$ reaching ~2.1 μ_B per cell at 2 K, decreasing to ~1.6 $\mu_{\rm B}$ per cell at 80 K. These results are manifestly divergent from the geometrically frustrated AFM order of the LuMnO3 matrix below TN, which typically imply $|\mu|_{\text{cell}} = 0.5$ A schematic view of the calculated unit cell and the magnetic lattice at 2 K is presented in Fig. 4. The calculated $\langle \mu \rangle \sim 2.84 \,\mu_{\rm B}$ per Mn ion at 2 K does not reach the $\sim 3.2 \,\mu_{\rm B}$ per Mn ion reported for the strict stoichiometric compound, neither the integral ionic state of Mn^{3+} (4.9 μ_B).⁵ This reduction is attributed to the slight charge dislocation and adjustments in the covalent bonds of the self-doped compound due to Mn deficit ($\sim 2\%$). Fig. 5 shows the temperature dependence of the calculated magnetic parameters in the unit cell determined from the refinement of NPD patterns. These adjustments are associated with the magneto-elastic coupling between structural tunings and spin fluctuations of the system, enabling lower energy ground states at a given temperature.^{6,20,21}



Fig. 4 Structural and magnetic lattice representation of the LuMn0.98O $_3$ compound derived from NPD data collected at 2 K.

The local electronic perturbations (approximately 1 Mn vacancy in 8 cells for the LuMn_{0.98}O₃ compound) can act as pinning dwells for domain walls or even magnetic clusters^{22,23} and, although randomly dispersed throughout the solid, are not necessarily independent. In fact, those defects are embedded in a non-centrosymmetric crystallography host cell, which has an inherent ferroelectric character. Hence any noncompensated spin currents besides prompting additional polarization components are also deflected and aligned by the host charge gradient.⁵ Thus, such supplementary long range order is multiferroic and relies on the disruption of the delicate balance of the geometrically frustrated AFM matrix.²⁴ Other topological defects like crystallographic imperfections, grain and domain wall boundaries also disturb locally charge and magnetic symmetries and can also contribute to multiferroic properties.²⁵ In such complex non-collinear and weak ferromagnetic systems, the magnetoelectric effect can be evaluated by the interplay of anisotropy and the appearance of ferroelectricity due to spin currents as described by the Dzyaloshinskii-Moriya model.²⁶⁻²⁸ In the particular case of the system under study, the



Fig. 5 Temperature dependence of the magnetic moment projections $(\Sigma \mu_{x}, \Sigma \mu_{y}, \Sigma \mu_{z})$, unit cell magnetic moment $(|\mu|_{/cell})$ and average magnetic moment per Mn ion $(\langle \mu \rangle_{/Mn})$ in the hexagonal cell calculated from NPD.

basal electric polarization $P_{xy}(S_i)$ originating from a regular triangular geometry of spins S_i is related with

$$P_x(S_i) = K_S[S_1 \cdot (S_2 + S_3) - 2S_2 \cdot S_3] \text{ and } P_y(S_i) = 3^{1/2} K_S[S_1 \cdot (S_2 - S_3)]$$
(1)

where the coefficient $K_{\rm S} = 4.3^{1/2} \cdot e \cdot d \cdot (t/U)^3$ can be considered as a constant related to the average distance *d* between Mn sites, *t* is a hopping term and *U* the Coulomb interaction.⁹ By substituting $S_{\rm i} = (2m_{\rm e}/e \cdot \hbar) \cdot \mu_{\rm i}$ and adjusting the coefficient as $K_{\mu} = (2m_{\rm e}/e \cdot \hbar) \cdot K_{\rm S}$, it is possible to perform a straightforward comparison between the basal components of electric polarization resulting from the different magnetic configurations, as represented in Fig. 6.

The magnetic configuration schematized in Fig. 6a calculated for the self-doped LuMn_{0.98}O₃ compound at 2 K gives rise to a relevant component $P_{xy}(\mu_i) \sim 24.5 K_{\mu}$. This result stands for a colossal ~300% increase of the polarization in the basal plane, compared to the value arising from AFM frustrated spins in curled geometry represented in Fig. 6b; on the other hand, no polarization is expected from a ground state configuration with spins aligned along the vertices of the triangles represented in Fig. 6c. In Fig. 7 is presented the temperature dependence of the polarization components per unit cell only due to spin contribution. The temperature dependence of the magnitude of $P_x(\mu_i)$ apparently follows the behavior of the magnetization component



Fig. 6 Comparison of magnetic configurations assuming $\langle \mu \rangle_{/Mn} = 2.84 \ \mu_B$ (arrows) and respective electric polarization basal orthogonal components. Bold and shaded symbols represent the Mn ions in two stacking planes.



Fig. 7 Temperature dependence of the calculated electric polarization basal components in the unit cell due to spin contribution following the model described in ref. 9.

 $\Sigma \mu_z$ displayed in Fig. 5, having a noteworthy anomaly at 50 K and disappearing above the Néel temperature.

In order to further support the incidence of an enhanced ME effect on the self-doped $LuMn_{0.98}O_3$ compound, we resort to DFT to calculate the influence of the non-collinear magnetic order on the polarization. First, we considered non-magnetic control simulations in the ferroelectric and paraelectric configurations by using the same experimental lattice parameters found at 2 K.

The effective spontaneous polarization was calculated using the Berry-phase method included in the VASP code,³⁰ with respect to the paraelectric structure of space group P63/mmc. The spontaneous polarization for the P63cm non-magnetic case has only a z component as expected, estimated at 14.9 μ C cm⁻² $(33.4 \,\mu\text{C cm}^{-2} \text{ from the Berry-phase calculation and } -18.5 \,\mu\text{C cm}^{-2}$ from the ionic contribution). This value is higher than those obtained with magnetic orders, similar to a previous calculation with non-magnetic HoMnO₃.³¹ To evaluate the effect of magnetic configurations on the polarization we included the experimental non-collinear order in calculations while keeping the same paraelectric and ferroelectric structures. By comparison to the centrosymmetric structure, the spontaneous polarization remains zero along the z axis. Nonetheless in the presence of the magnetic structure a polarization appears in the *xy* plane, with P = (-2.91, -2.91)-2.42, 0.00) μ C cm⁻². For the ferroelectric structure refined from NPD data obtained at 2 K, the DFT simulated polarization becomes $P = (-0.52, 0.33, 4.62) \mu C \text{ cm}^{-2}$ considering the directions of the atomic moments constrained while the magnitude of the moments was allowed to converge. A similar value of $P = (-0.47, 0.32, 4.65) \ \mu C \ cm^{-2}$ can be obtained when the magnitude of the magnetic moments is constrained. Although the intrinsic z component is reduced, the appearance of the basal components now accounts for nearly 13% of the total polarization originated only from the magnetic structure.

In Fig. 8a some pertinent anomalies of the magnetization of the LuMn_{0.98}O₃ compound can be observed. The differential curve²⁹ enables one to point the main magnetic transition around the expected $T_{\rm N} \sim 90$ K and noteworthy anomalies between 20 and 50 K respectively. Furthermore, the frustration parameter $\Theta_{\rm CW}/T_{\rm N}^{-5}$ for the self-doped sample LuMn_{0.98}O₃ reaches a much higher ~5.9 ratio than the value ~4.2 of the strict stoichiometric compound. As discussed previously in ref. 7 in the LuMn_{0.98}O₃ sample the Mn³⁺ ions appear to be strongly correlated even up to 330 K, with calculated $\langle \mu_{\rm eff} \rangle \sim 5.6 \ \mu_{\rm B}$ per Mn well above $T_{\rm N}$, most likely due to frozen complex (local) magnetic cluster-like behavior. However, magnetic measurements as a function of magnetic field above 100 K evidence a paramagnetic response.⁷

In order to unveil the origin of these anomalies we performed Raman spectroscopy measurements in the same sample, covering in detail the lower temperature range and not only focused on the main AFM/PM transition (~90 K).^{32,33} Among the Raman active modes observed the analysis is focused on the temperature dependence of the main A₁ mode (~685 cm⁻¹ at T = 300 K), assigned to the symmetric stretching vibrations of Mn–O bonds, which is known to be very sensitive to structural distortions and magnetic ordering.³⁴ In fact, the variations of



Fig. 8 Comparison of response of the LuMn_{0.98}O₃ sample with temperature: (a) $\partial M/\partial T^7$ and (b) A₁ Raman resonant mode. Inset: Details of the different behaviors in the temperature range 10–50, 50–90, 100–120 and 130–150 K respectively traced with different colored dotted lines.

the Mn-O bond distance affect the superposition of orbitals and consequently the superexchange integrals. Fig. 8b presents the temperature dependence of the A₁ mode wavenumber ($\omega(T)$), while the respective inset presents a zoom-in view of the temperature range between 10 and 150 K and enables one to draw a parallel with some magnetic variations observed in the curve of Fig. 8a. The PM/AFM phase transition is well signalized by clear changes in $\omega(T)$ and $\partial M/\partial T$ slopes at $T_{\rm N} \sim 90$ K. Moreover, other clear anomalies are observed at 50 K configuring the occurrence of structural distortions, most likely due to readjustments on the complex spin structure.33 Such rearrangements at 50 K are also corroborated by the structural distortion perceived from the NPD data analysis, hence evidencing a relevant spin-phonon coupling in the compound. Furthermore, the changes in the slope of the A_1 mode wavenumber above T_N clearly deviate from the conventional nonlinear decay due to thermal processes, as found above 160 K up to 350 K. The increase of $\omega(T)$ between 130 and 110 K suggests a precursor effect of the AFM phase transition.³⁴ On the other hand, the decrease of $\omega(T)$ between 150 and 130 K suggests the nucleation of disperse ferromagnetic contributions³⁴ in agreement with the relatively high $\langle \mu_{\text{eff}} \rangle$ and compatible with the presence of magnetic clusters.

Further correlation between the magnetic and structural properties can be found in the temperature dependence of the real (ε_r') and imaginary (ε_r'') part of the relative electric permittivity, measured at 1.0 MHz in the range between 10 and 150 K, as shown in Fig. 9a and b respectively. Above 150 K ε_r' and ε_r'' responses show a regular increase with temperature becoming dominated by thermal processes above 275–300 K.



Fig. 9 Details of the temperature dependence of the (a) real (ε_r ') and (b) imaginary (ε_r ") parts of the relative electric permittivity at 1.0 MHz in the range between 10 and 150 K. (c) Pyroelectric current under 1526 V cm⁻¹ poling and 7 K min⁻¹ heat rate. (d) Variation of polarization (ΔP) integrated from pyro-electric current.

In addition, pyroelectric current measurements were performed after poling the sample with 1526 V cm⁻¹ electric field and a 7 K min⁻¹ heating run. Fig. 9c shows the temperature dependence of the pyroelectric current in the noteworthy region between 10 and 140 K, since the pyroelectric current is also dominated by thermal processes above ~ 150 K. Subsequently, Fig. 9d shows the electric polarization variation (ΔP) obtained by the time integration of the pyroelectric current. The data presented in Fig. 8 and 9 corroborate and unambiguously signalize the AFM transition at $T_{\rm N}$ = 92 K, and the curves exhibit small anomalies observable at 30-50 K and even more relevant anomalies at 120-140 K. Such anomalies are associated with structural distortions and spin rearrangements leading to variations of ε and ΔP with temperature.^{33,35} The results obtained by NPD also substantiate the existence of a broader range of complex multiferroic phases in this self-doped compound when compared to the stoichiometric one.

Conclusions

The LuMn_{0.98}O₃ hexagonal compound was studied in detail through independent magnetic, dielectric, pyroelectric and Raman measurements which consistently revealed pertinent anomalies in response curves near analogous temperature regions: besides the expected main magnetic transition at 92 K, significant variances were also detected between 30–50 K and 120–140 K, configuring correlated polar, magnetic and structural rearrangements. Relevant NPD results describe a non-cancelled magnetic structure within the crystallographic cell below T_N , confirming a significant perturbation of the magnetic triangular ordering attributed to the strict stoichiometric compound while preserving the inherent crystallographic ferroelectricity. Moreover, this novel magnetic arrangement led to the appearance of an additional specific electric polarization component in the basal plane, also confirmed by *ab initio* DFT theory calculations. By breaking the antiferromagnetic geometric frustration found in LuMnO₃ and prompting a ferromagnetic contribution in the LuMn_{0.98}O₃ compound we validate the existence of a novel FM + FE type I multiferroic state and demonstrated that material modification by self-doping is also a valid experimental approach to develop multiferroic properties and enhance magnetoelectric effects, aiming to progress our understanding and potentialities for technological applications.

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