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Ferroelectric-ferroelectric phase coexistence in $Na_{1/2}Bi_{1/2}TiO_3$

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Morphotropic phase boundary (MPB) systems are characterized by the coexistence of two ferroelectric phases and are associated with anomalous piezoelectric properties. In general, such coexistence is brought about by composition induced ferroelectric-ferroelectric instability. Here we demonstrate that a pure ferroelectric compound $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) exhibits the coexistence of two ferroelectric phases, rhombohedral ($R3c$) and monoclinic (Cc), in its equilibrium state at room temperature. This was unravelled by adopting a unique strategy of comparative structural analysis of electrically poled and thermally annealed specimens using high resolution synchrotron x-ray powder diffraction data. The relative fraction of the coexisting phases was found to be highly sensitive to thermal, mechanical, and electrical stimuli. The coexistence of ferroelectric phases in the ground state of the pure compound will have significant bearing on the way MPB is induced in NBT-based lead-free piezoceramics.

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The past few years have witnessed a great surge in research related to lead-free ferroelectrics. In view of the well-established correlation between the enhanced piezoelectric properties and the morphotropic phase boundary (MPB) in lead-based ferroelectric systems such as $Pb(Zr,Ti)O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, and $Pb(Mn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, there is increasing emphasis on lead-free ferroelectric systems exhibiting features of MPB. The systems $KNbO_3$-$NaNbO_3$ (KNN)[1–4] and modified $Na_{1/2}Bi_{1/2}TiO_3$ (NBT)[5–10] have received significant attention in this regard. However, as compared to the lead-based piezoelectrics, for which the mechanism of enhanced piezoelectric response is relatively well understood in terms of the polarization rotation model,[11–13] structure-property correlations in lead-free systems are far from settled. For example, the most fundamental factor which stands in the way of establishing a comprehensive structure-property correlation in NBT-based piezoelectrics is related to the fact that the ground state structure of the parent compound, NBT, itself is not yet settled even six decades after its discovery by Smolenskii *et al.*[14] The traditional view of the structure and phase transition behavior of this compound has been summarized in the work of Jones and Thomas,[15] who suggested the following sequence of transitions:

$$R3c \overset{523\text{ K}}{\leftrightarrow} R3c + P4bm \overset{670\text{ K}}{\leftrightarrow} P4bm \overset{813\text{ K}}{\leftrightarrow} Pm3m.$$

Subsequent to this work, there has been growing evidence about the departure from the rhombohedral structure at room temperature. Based on a neutron diffuse scattering study, Balagurov *et al.*[16] postulated the occurrence of a one-dimensional modulation and the possibility of ordering of Na and Bi ions. Cation ordering was also proposed by Petzelt *et al.*[17] to explain their IR and Raman spectra. Kreisel *et al.*,[18] on the other hand, proposed the existence of Guinier-Preston zones (GPZs) to interpret diffuse scattering rods in x-ray diffuse scattering. Later, a local structure analysis using an x-ray absorption fine structure (XAFS) study suggested the monoclinic structure of the GPZs.[19] Very recently a bifurcated polarization rotation model in NBT has been postulated using a neutron pair distribution analysis.[20] Electron diffraction studies, on the other hand, have suggested another aspect of departure from pure rhombohedral symmetry.[21,22] These studies have shown that NBT exhibits localized in-phase $(+)$ octahedral tilts in the otherwise average $a^-a^-a^-/a^-a^-c^-$ tilt present in the system. The two alternative views which have emerged from the electron diffraction studies are as follows: (i) The room temperature phase of NBT is a two-phase mixture with the major phase being rhombohedral (space group $R3c$, $a^-a^-a^-$ tilt system) along with small tetragonal platelets (space group $P4bm$, $a^0a^0c^+$ tilt system),[21] or (ii) the structure consists of nanoscale domains that feature very short range $a^-a^-c^+$ tilts (1–3 nm) interspersed in between the relatively long range $a^-a^-c^-/a^-a^-a^-$ tilts (10–40 nm).[22] This short range alteration in the tilt takes place across pseudocubic $\{100\}_{pc}$ twin domain boundaries. In the latter model, such an assemblage of octahedral disorder would result in an average out-of-phase tilting along any octahedral chain, and yield a pseudorhombohedral/monoclinic structure. The average monoclinic symmetry (Cc) for NBT was first proposed by Gorfman and Thomas using a single crystal structure analysis.[23] Later, Aksel *et al.*[24] demonstrated the insufficiency of the $R3c$ model to fit the synchrotron x-ray powder diffraction pattern. Though the authors showed a relatively better fit with the Cc model, in a subsequent publication they acknowledged that the fit with the Cc model was not entirely satisfactory and attributed the discrepancies to the presence of local disorder in the system.[25] In another interesting development, Rao and Ranjan[26] demonstrated that the x-ray powder diffraction pattern of electrically poled NBT could be nicely fitted with the pure rhombohedral ($R3c$) structural model without the need to postulate any disorder in the system. The authors have argued about the possibility of an electric field driven monoclinic to rhombohedral irreversible transformation.[26] This field dependent irreversible transformation provided an opportunity to resolve the complexity associated with the ground state structure of NBT. By adopting a strategy of comparative structure analysis using the high resolution synchrotron x-ray diffraction (XRD) data of electrically poled and annealed specimens of NBT, it became possible to unravel unambiguously the coexistence of two ferroelectric phases, monoclinic (Cc) and rhombohedral ($R3c$), in the equilibrium

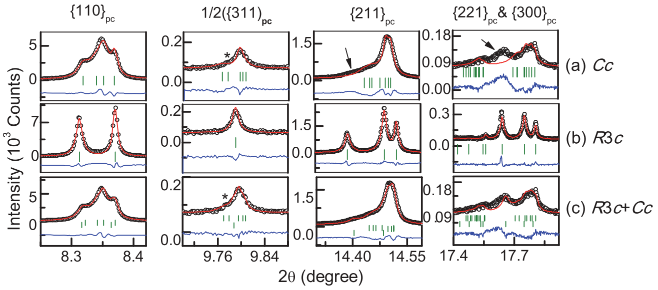

FIG. 1. (Color online) Rietveld fits of synchrotron x-ray powder diffraction patterns of (a) annealed NBT fitted by monoclinic Cc, (b) poled NBT with the $R3c$ model, and (c) annealed NBT with $Cc + R3c$ phase coexistence models. The observed pattern is represented by open circles and the fit is represented by a continuous line. The Bragg peak positions are shown with vertical bars. In (c), the lower vertical bars represent the $R3c$ phase. * indicates the weak hump in the superlattice reflection.

state at room temperature. This important finding also resolved the significant change observed in the diffraction patterns after thermomechanical treatment of NBT, as reported very recently by Levin and Reany,[22] and provides the background for a detailed understanding of the evolution of MPB in NBT-based lead-free piezoelectrics.

Ceramic specimens of NBT were prepared by a conventional solid state route. Dried oxides of high purity reagent grade Bi_2O_3, Na_2CO_3, and TiO_2 were used as raw materials. Stoichiometric amounts of the oxides were mixed in a planetary ball mill for 10 h with acetone as the mixing medium using zirconia bowls and balls. After drying, the mixed powders were calcined at 900 °C for 2 h in an alumina crucible. The calcined powders were then mixed with 2% polyvinyl alcohol (PVA) and pressed into pellets of 15 mm diameter and 1.5 mm thickness by uniaxial pressing at 250 MPa. These pellets were finally sintered in air at 1140 °C for 3 h. The pellets were polished to remove about 0.2 mm of the ceramic from the surface before using for any measurements. Poling was done at room temperature in silicone oil by applying a dc electrical field of 70 kV/cm for 10 min on sintered pellets. A Precision Premier II tester (Radiant Technologies, Inc.) was used to obtain the P-E loop measurements. The piezoelectric coefficient d_{33} was measured using a Berlincourt meter from Piezotest (model PM300). As mentioned before,[26] diffraction data for the structure analysis were collected on powder specimens to avoid preferred orientation. The European Synchrotron Radiation Facility (ESRF) with beamline ID30 was used to obtain the synchrotron data for the unpoled sample annealed at 600 °C for 2 h and the sample poled at 70 kV/cm for 10 min, with a step size of 0.002° using a wavelength of 0.399 91 Å. The rest of the powder x-ray diffraction patterns were collected from a laboratory Bruker powder diffractometer (model D8 Advance) using a Cu $K\alpha$ x-ray source. Rietveld refinements were carried out using the FULLPROF package.[27] The refined parameters include 2θ-zero, background fitted by linear interpolation, lattice parameter, atomic coordinates, thermal displacement parameters, and the pseudo-Voigt profile shape parameters.

Figure 1(a) shows a Rietveld fit of the high resolution synchrotron x-ray diffraction pattern of annealed (600 °C for 2 h) NBT powder with the recently proposed monoclinic Cc structural model. In order to provide visual clarity, only some of the representative pseudocubic Bragg peaks have been shown on a magnified scale. Also, for the sake of direct comparison, the fitted pattern of the poled specimen with the rhombohedral structural model ($R3c$) is shown in Fig. 1(b). It is obvious from this figure that while the pattern of the poled specimen fits very well with the $R3c$ model, the fitting of the annealed pattern with the Cc model is relatively unsatisfactory [Fig. 1(a)]. For example, the best fit obtained with the Cc model fails to account for the shoulder observed at 14.4° and also a weak peak at 17.65°. Both of these misfit regions have been marked with arrows in Fig. 1(a). The set of peaks at these 2θ positions belong to the family of $\{211\}_{pc}$ and $\{221/300\}_{pc}$ pseudocubic reflections, respectively. Aksel *et al.*[25] have also reported the inability of the Cc model to account completely for the diffraction pattern and attributed this to some kind of local disorder inherent in the system. Though the presence of disorder in the system may not be ruled out, that it can lead to peaks such as those shown by the two arrows in Fig. 1(a) seems very unlikely. We rather suspected that the additional peaks marked with arrows in Fig. 1(a) could be a manifestation of another phase in the system. Interestingly, the clue to the nature of the second phase becomes evident on comparison of Figs. 1(a) and 1(b)—the rhombohedral phase exhibits characteristic peaks at nearly the same 2θ positions as the unexplained peaks (marked by arrows). This implies that the equilibrium state of NBT at room temperature consists of a coexistence of $R3c$ and Cc phases. As a matter of fact, we also considered other plausible two-phase models, namely, (i) tetragonal $(P4bm) + R3c$, (ii) monoclinic $(Cm) + R3c$, and (iii) monoclinic $(Pm) + R3c$. The rationale for the first model $P4bm + R3c$ was motivated by the fact that electron diffraction studies of NBT have revealed the presence of $a^0a^0c^+$ octahedral tilt, which has traditionally been described in terms of the tetragonal $P4bm$ structure.[15] The $Cm + R3c$ model was guided by the local structure analysis of NBT by Petzelt *et al.*,[17] which suggested the presence of localized monoclinic (Cm) distortion. For the sake of completeness, we also considered another monoclinic phase (Pm), which is known to occur in ferroelectric systems exhibiting a morphotropic phase boundary such as the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ system.[28] In the three models mentioned above, the observed superlattice reflections due to out-of-phase tilt of oxygen octahedra should solely be accounted for only by the $R3c$ phase. It was found that the different two-phase models could account for the main Bragg peaks equally well. But none of them could satisfactorily fit the superlattice reflection $1/2\{311\}_{pc}$. A close examination of this superlattice reflection revealed a weak but noticeable hump on its left side (indicated by * in Fig. 1). This suggests more than one Bragg peak near this 2θ position. And since the $R3c$ model predicts only one Bragg peak at this position, the profile of the $1/2\{311\}_{pc}$ superlattice reflection obviously could not be fitted satisfactorily. This profile is fitted relatively better by the single-phase Cc model, but, as noted above, the Cc model in itself cannot account for the two additional peaks marked with arrows in Fig. 1(a). The detailed analysis therefore suggested $Cc + R3c$ to be the most suitable phase coexistence model to describe the equilibrium state of NBT at room temperature. It may be remarked that the subtle features

TABLE I. Structural parameters of annealed NBT obtained by Rietveld refinement of synchrotron powder diffraction data with the $Cc + R3c$ space group model.

	Cc				$R3c$			
	x	y	z	B (Å^2)	x	y	z	B (Å^2)
Na/Bi	0	0.25	0	4.26(16)	0	0	0.2770(9)	2.5(4)
Ti	0.2633(13)	0.252(2)	0.7893(12)	0.60(8)	0	0	0.0120(13)	1.7(5)
O1	0.020(5)	0.199(2)	0.562(7)	0.2(5)	0.1173(16)	0.333(3)	0.08330[a]	1.1(8)
O2	0.191(2)	0.480(4)	2.8(7)	0.8(7)				
O3	0.231(3)	0.987(4)	0.030(6)	1.1(7)				
	$a = 9.519\,66(15)$, $b = 5.479\,79(6)$, $c = 5.511\,41(13)$, $\beta = 125.2776(13)^\circ$, phase fraction = 83 (% vol)				$a = b = 5.484\,10(11)$, $c = 13.5476(4)$, $\gamma = 120^\circ$, phase fraction = 17 (% vol)			
	$R_{\mathrm{wp}} = 6.402$, $R_{\mathrm{exp}} = 9.339$							

[a] z coordinate of O in the $R3c$ phase is fixed to take care of the floating origin.

reported above could not be clearly seen in laboratory x-ray diffraction data and hence it was not possible to arrive at a unique phase coexistence model. At the same time, mere high resolution diffraction data of the annealed NBT was unable to provide the clue for the existence of the $R3c$ phase.

It may be remarked that since the lattice distortions of the coexisting phases (with respect to the ideal cubic structure) are small, the Bragg profiles of both the phases considered in the analysis overlap considerably. Since, in general, such situations often lead to nonconvergence of the refinement, a constrained refinement strategy was adopted to begin with. Since visual inspection revealed that the Bragg positions of the rhombohedral phase (poled specimen) coincide with those with the unexplained peaks in Fig. 1(a), the lattice and the structural parameters of the $R3c$ phase were fixed in the beginning at the values obtained for the poled NBT. The rhombohedral structural parameters were relaxed only after the parameters of the Cc phase were sufficiently refined to improve the overall fit. The refined structural parameters of the annealed specimen with the $R3c + Cc$ model are summarized in Table I. It was found that the refined structural parameters of the $R3c$ phase in the unpoled specimen are very close to that in the poled specimen. For example, the lattice parameters of the rhombohedral phase ($a = 5.480$ Å, $c = 13.564$ Å) in the poled specimen are very close to the refined rhombohedral lattice parameters in the annealed specimen ($a = 5.484$ Å, $c = 13.547$ Å). This feature may be taken as a confirmation of the $Cc + R3c$ phase coexistence model—the pattern of the annealed specimen merely required a certain fraction of the $R3c$ phase to account for the features which was not possible using single-phase Cc parameters. We may mention that the XRD patterns obtained after annealing the poled specimens at 400 °C [Fig. 2(g)] and 700 °C [Fig. 2(h)] are similar to the pattern of the unpoled specimen annealed at 600 °C [Fig. 2(a)]. This repeated reproducibility of the XRD patterns after annealing confirms that the annealed specimen truly represents the equilibrium state of NBT at room temperature and that even 400 °C is sufficient for annealing. It appears that the effect of mechanical impact and electric field induced structural changes required the system to be in a ferroelectric state, and that heating the system above the Curie point erases the memory of the structural changes in this state and restores the equilibrium structural features of the system when cooled to room temperature.

The conclusion with regard to the coexistence of two ferroelectric phases arrived above provides the appropriate background for understanding the origin of the changes in diffraction patterns of NBT after different mechanical and thermal treatments, reported recently.[22] We recorded our own (laboratory) x-ray powder diffraction patterns after subjecting NBT to different thermal, mechanical, and also electrical field treatments (Fig. 2). In conformity with what has been reported in Ref. 22, the shapes of the peaks are different for different cases. It is interesting to note that the pattern of specimen ground for 30 min [Fig. 2(c)] is nearly identical to the pattern of the specimen poled at 25 kV/cm [Fig. 2(d)]. This implies that, though treated differently, both the specimens have identical structural features. Since the pattern of the 40 kV/cm poled sample can be fitted very well with a single-phase $R3c$ model, and also that the pattern evolved gradually towards the pure rhombohedral phase with increasing field in the range 0–40 kV/cm, we fitted all the patterns in Fig. 2 with the $R3c + Cc$ phase coexistence model. The initial structural parameters of the coexisting phases were taken from Table I. This phase coexistence model was able to fit all the patterns

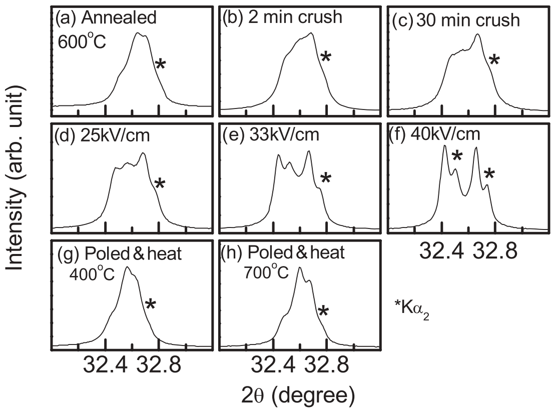

FIG. 2. X-ray powder diffraction pattern of the pseudocubic $\{110\}_{\mathrm{pc}}$ peak after (a) heating the specimen at 600 °C, (b) manual grinding for 2 min, (c) grinding for 30 min, (d) poling at 25 kV/cm, (e) poling at 33 kV/cm, (f) poling at 40 kV/cm, (g) poling at 70 kV/cm and then the crushed powder is annealed at 400 °C for 30 min, and (h) poling at 70 kV/cm and then the crushed powder is annealed at 700 °C for 6 h.

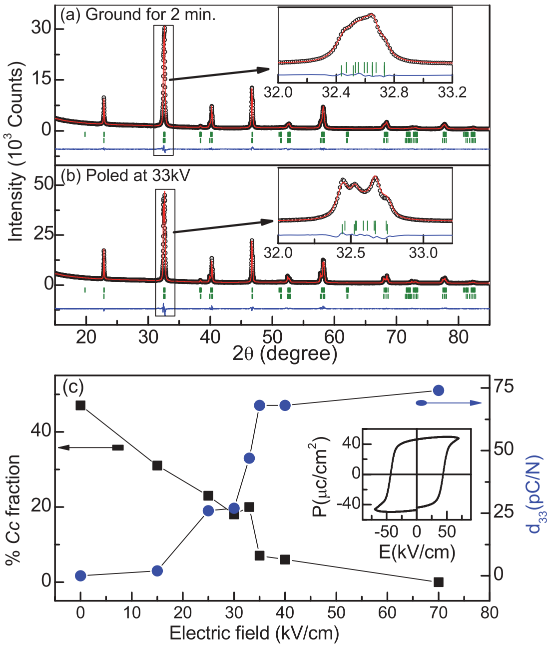

FIG. 3. (Color online) Rietveld plot of XRD pattern of NBT powder (a) crushed for 2 min and (b) poled at 33 kV/cm. Both the patterns were fitted with the $Cc + R3c$ coexistence model. The observed pattern is represented by open circles and the fit is represented by a continuous line. The Bragg peak positions are shown with vertical bars. The lower vertical bars represent the $R3c$ phase. (c) Variation of the fraction of the monoclinic phase and longitudinal piezoelectric coefficient (d_{33}) as a function of the poling field.

shown in Fig. 2 very well with a varying fraction of the $R3c$ phase. Figure 3 shows the Rietveld fitted patterns of two representative cases: one ground for 2 min and the other poled at 33 kV/cm. The relative volume fraction of the $R3c$ phase increased from ~17% to ~53% on simple manual grinding of the annealed powder for 2 min. It was noted that additional grinding for 30 min more increased the $R3c$ fraction to ~65%. Increasing the ground time further did not change the profile shape, thereby suggesting that the impact induced monoclinic to rhombohedral transformation remains partial. It is now obvious that the various profile shapes reported by Levin and Reany,[22] some of which are identical to ours, are a consequence of varying the relative fraction of the $R3c$ and the Cc phases in the differently treated specimens. For the electric field treated specimens, the variation of the Cc volume fraction as a function of the poling field is shown in Fig. 3(c). It should be noted that in this plot, for the sake of consistency, we have given the phase fraction of the zero-field poled (unpoled) specimen after crushing (and not of the annealed specimen) and hence the $R3c$ phase fraction appears as 50% instead of ~17%. The poled specimens cannot be annealed since the information related to the irreversible structural changes due to poling in the ferroelectric state would be lost after annealing. Above 35 kV/cm, which also happens to be close to the coercive field of NBT [Fig. 3(c) inset], the specimen exhibits a nearly pure rhombohedral phase. It appears that above this field, the electric field induced irreversible structural change overwhelms the system and the mechanical impact (for example, manual crushing of the pellet to powder) induced changes become secondary in nature. Figure 3(c) shows the variation of the Cc phase fraction and the longitudinal piezoelectric coefficient d_{33} with poling field. It is interesting to note that d_{33} follows the same trend with field as the volume fraction of the rhombohedral phase. Since the trend in d_{33} is a measure of the alignment of the ferroelectric domains in the poling direction, it follows that the electric field plays a dual role of transforming the monoclinic phase regions to rhombohedral and at the same time aligns the domains of the rhombohedral phase along the field direction.

Although we have shown evidence of $R3c + Cc$ phase coexistence at room temperature in NBT, and also the fact that the electric field irreversibly transforms the monoclinic phase to rhombohedral, it remains an open question as to how these two phases appear at room temperature in the first place. The coexistence of ferroelectric phases has so far been reported only for ferroelectric solid solutions exhibiting a morphotropic phase boundary such as $Pb(Zr_{1-x}Ti_x)O_3$, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$(x)PbTiO_3$, and similar systems.[11–13,28] In such systems, for a certain narrow range, the ferroelectric-ferroelectric instability brings about flattening of the anisotropic energy profile in the system, leading to the coexistence of phases with an associated high piezoelectric response. A simple analogy with these well-known MPB systems may suggest that the occurrence of $R3c + Cc$ could be a manifestation of inherent competing ferroelectric-ferroelectric instability in NBT close to room temperature. If this is true, then NBT seems to be an exception, since such a feature has yet to be reported experimentally for pure ferroelectric compounds. A first principles study, though, has suggested that MPB can be induced even in sufficiently compressed $PbTiO_3$.[29] Alternatively, realizing the fact that the NBT passes through intermediate tetragonal and orthorhombic (*Pbnm*) phases in its paraelectric state, with both the phases coexisting in a certain temperature interval around 300 °C,[30] it is also likely that the paraelectric tetragonal and the paraelectric orthorhombic phases may transform separately to two ferroelectric phases $R3c$ and Cc, respectively, as the system cools down to room temperature. If the latter scenario is correct, the existence of two ferroelectric phases is merely a coincidence resulting from this peculiar type of phase transition. A more detailed study would be required to sort out these issues.

In conclusion, we have demonstrated that the lead-free ferroelectric $Na_{1/2}Bi_{1/2}TiO_3$ exhibits coexistence of two ferroelectric phases $R3c$ and Cc in its equilibrium state at room temperature. The relative fraction of the coexisting phases is highly susceptible to thermal, mechanical, and electrical stimuli. While mechanical and electrical stresses drive the system away from the equilibrium situation by increasing the fraction of the rhombohedral phase, annealing the system tends to restore the equilibrium ratio of the phases. The structural disorder suggested by different experimental groups in the past seems to be related to the lack of knowledge with regard to the nature of phase coexistence in this system. We suggest that the MPB-like feature in NBT is accidental and related to the fact that two crystallographically different paraelectric states, tetragonal and orthorhombic, transform independently to two ferroelectric phases; and is not related to flattening of the anisotropic energy profile of the system due to ferroelectric-ferroelectric instabilities. In view of the fact, that the parent compound NBT itself shows coexistence of ferroelectric phases, the very nature of the evolution of MPB in the NBT-based lead-free piezoelectric systems such as NBT-$BaTiO_3$ and NBT-$(K_{1/2}Bi_{1/2})TiO_3$ requires reexamination.

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