



# X-ray analysis of phase coexistence and electric poling processing in alkaline niobate-based compositions

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## ABSTRACT

The characteristic and origin of two-phase coexistence and the content of each phase in typical alkaline niobate-based lead-free compositions were investigated through the refinement of X-ray diffraction peaks and the measurement of dielectric constant versus temperature curves. The diffuse nature of polymorphic phase transition has resulted in the coexistence of two ferroelectric phases within a wide composition and temperature range. As a result, the optimum piezoelectric properties appear in the composition rich in tetragonal phases and there is a remarkable poling temperature effect. Discussions on the difference between morphotropic phase boundary and polymorphic phase boundary were made in combination with the variation of electrical properties.

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## 1. Introduction

It is well known that high piezoelectric responses in conventional Pb-based piezoelectric ceramics are attributed to a so-called morphotropic phase boundary (MPB) where two ferroelectric phases coexist [1,2]. It is defined as an abrupt change in phase structure due to a narrow composition variation, and thus nearly vertical to the composition scale [2]. The concept “MPB” was ever used in lead-free alkaline niobate-based systems for quite a while in a chronic manner [3–5]. However, it has recently been realized that the phase coexistence in these systems is formed simply by shifting a diffuse polymorphic phase transition (PPT) between orthorhombic and tetragonal phases downwards to around room temperature [6,7]. The movement of the PPT temperature ( $T_{0-t}$ ) is gradual and continuous with changing the composition, thus forming a nearly parallel line to the composition axis [8,9]. Therefore, a big difference in the slope of the phase boundary relative to the composition scale has induced extremely different temperature dependence of electrical properties in Pb-based and lead-free alkaline niobate-based compositions [7,10]. However, the mechanism concerning why/how the two-phase coexistence contributes to optimum piezoelectric properties in both cases looks similar; that is to say, increased number of spontaneous polarization vectors makes the domain switching easier along the direction of external electric field [11]. Recently, a polymorphic phase boundary (PPB) rather than an MPB has been suggested to describe this kind

of phase coexistence owing to “polymorphism”, instead of “morphotropism” [7,12]. However, it is impressed that there is still lack of deep analyses concerning the following two issues.

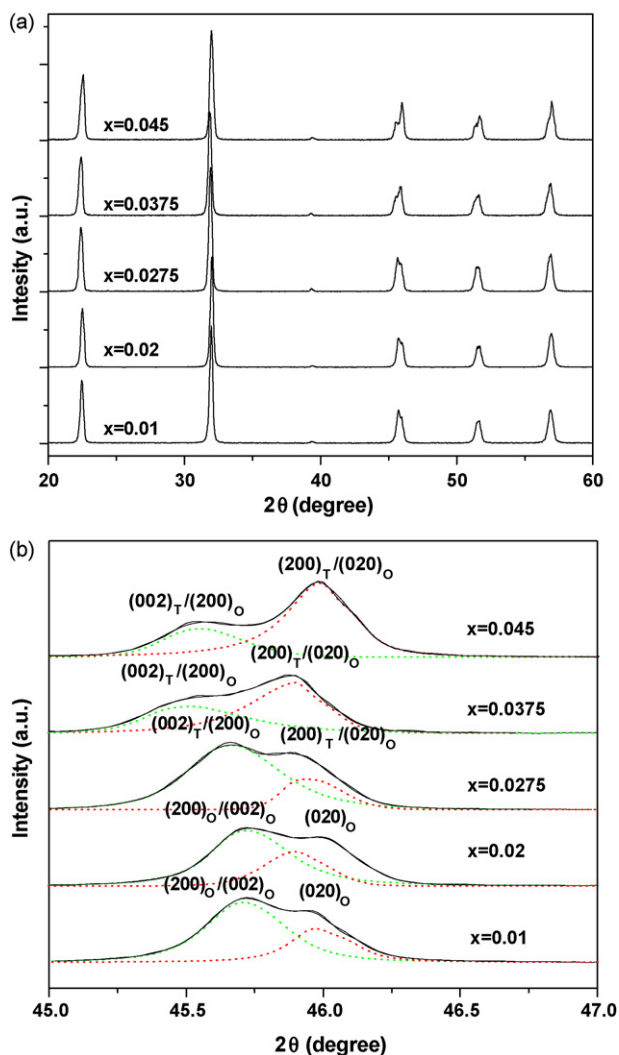
Firstly, the two-phase coexistence in alkaline niobate-based compositions needs detailed structural analysis. In this aspect, a lot of work has been done in Pb-based compositions like  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) materials by means of high-resolution X-ray diffraction (XRD) [13,14]. The width of phase coexistence zone in alkaline niobate-based systems was just vaguely estimated so far. Secondly, it would be of interest to explore the origin and characteristic of two-phase coexistence and the correlation with apparent electrical properties in alkaline niobate-based compositions. These studies might make sense for better understanding both composition and temperature dependences of electrical properties and further searching for a way to improve them.

The purpose of this study is thus to clarify the above two issues on the basis of typical lead-free compositions  $(\text{Na}_{0.52}\text{K}_{0.48-x})(\text{Nb}_{0.92-x}\text{Sb}_{0.08})\text{O}_3-x\text{LiTaO}_3$  (NKNS-xLT) as a case material. The quantitative XRD analysis was carried out by means of a Rietveld method for identification of phase coexistence and calculation of phase content. The response of dielectric, ferroelectric and piezoelectric properties to both composition and temperature was discussed in combination with the PPB.

## 2. Experimental

NKNS-xLT ceramics ( $0.01 \leq x \leq 0.045$ ) were manufactured by a conventional solid state method. The detailed processing procedures could be referred to our previous work [7]. Disk pellets of each composition were sintered at optimum temperatures. Fired-on silver paste was used as electrodes for electrical measurement. The samples were poled at different temperatures for 30 min under a dc field of 3 kV/mm and cooled to room temperature by maintaining the electric field.

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**Fig. 1.** The XRD patterns of NKNS-xLT compositions (a) and fitted (200) lines near  $2\theta = 46^\circ$  (solid lines denote original experimental results and dash lines fitted lines) (b).

Powder X-ray diffraction (XRD, D/Mzx-rB, Rigaku, Japan) patterns of crushed pellets were recorded using a Cu  $K\alpha 1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV at the scanning speed of  $4^\circ/\text{min}$ . Dielectric constant was measured as a function of temperature by an LCR meter (HP4284, USA) equipped with a temperature box filled with liquid nitrogen. The piezoelectric constant  $d_{33}$  was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planer electromechanical coupling factor  $k_p$  were determined by a resonance-antiresonance method with an impedance analyzer (PV70A, Beijing Band ERA Co., Ltd., China).

### 3. Result and discussion

Fig. 1(a) shows the XRD patterns of NKNS-xLT compositions. All patterns show typical characteristic diffraction peaks for a perovskite structure and the main difference between compositions can be easily detected in  $\{200\}$  reflection lines near  $46^\circ$ . To obtain precise phase analysis, the  $\{200\}$  reflection lines (solid lines) are fitted using Pearson-VII function as shown in Fig. 1(b). For the purpose to achieve correct compositions, all samples were covered during sintering with double crucibles using the protection atmosphere to reduce the volatilization of the components. It can be seen that the increase of LT content has induced an orthorhombic-tetragonal phase transition at room temperature. However, distinct phase boundary is hard to identify probably because the phase coexistence between orthorhombic and tetragonal phases (totally four peaks for (200) diffraction lines) could

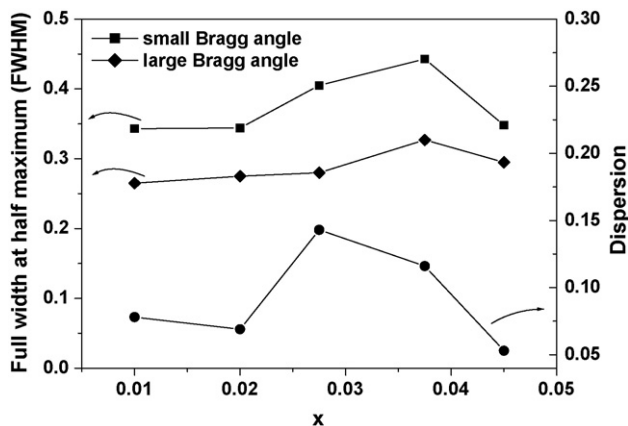
**Table 1**

Correlation between real intensity of (200) peaks, intensity sum of diffraction peaks concerning each kind of phase and the phase content.

	Compositions (x)				
	0.01	0.02	0.0275	0.0375	0.045
$I_{\text{Small-Brag}}$	1311	1173	1110	950	783
$I_{\text{Large-Brag}}$	1053	992	1032	1168	1519
$SI_T$	795	811	954	1386	2256
$SI_O$	1569	1355	1188	732	47
$F_T$ (%)	33.6	37.5	44.5	65.4	98.1

be more complex than that between rhombohedral and tetragonal ferroelectric phases in PZT-based systems (totally three peaks for (200) diffraction lines). The (200) peaks for tetragonal and orthorhombic phases overlap to a certain degree, which makes it difficult to separate one from another. It is known that an ideal cubic symmetry with  $a=b=c$  has only one diffraction peak (200). However, an orthorhombic symmetry with  $a \approx c > b$  is usually characterized by the splitting of (200)/(002) and (020) peaks owing to the difference between  $a$  and  $b$ . Compared to (020) line, the (200) line corresponding to a larger lattice constant has a smaller Bragg angle. Because of multiplicity factors, the intensity ratio of  $I(200)_O/I(020)_O$  for an orthorhombic structure ( $I(200)_T/I(002)_T$  for a tetragonal structure) is about 2. In addition, an ideal tetragonal symmetry with  $a=b < c$  is characteristic of split (200)/(020) and (002) peaks, and (002) line has a smaller Bragg angle. It can be seen from Fig. 1 that the intensity ratio of  $I(200)_O/I(020)_O$  decreases gradually with increasing  $x$  for compositions near orthorhombic side. Therefore, according to the real intensity values (Fig. 1) and multiplicity factor for compositions with coexistence of orthorhombic and tetragonal phases, the content of tetragonal phases ( $F_T$ ) can be calculated by the following equations:  $I_{\text{Small-Brag}} = 1/3SI_T + 2/3SI_O$ ,  $I_{\text{Large-Brag}} = 2/3SI_T + 1/3SI_O$ , and  $F_T = SI_T/(SI_T + SI_O)$  [15], where  $I_{\text{Small-Brag}}$  and  $I_{\text{Large-Brag}}$  are the intensities of (200) peaks with small Bragg angles and large Bragg angles, respectively, and  $SI_T$  and  $SI_O$  are the sums of peak intensities for tetragonal and orthorhombic phases, respectively, as summarized in Table 1. It can be found that the two-phase coexistence zone covers a broad composition range, which exhibits a different characteristic from that of an MPB.

The fitted (200) diffraction lines are used to calculate the full width at half maximum (FWHM) of the characteristic diffraction peaks, as shown in Fig. 2. On the one hand, it can be seen that the FWHM of the  $(200/002)_O$  peak (with smaller Bragg angle) for NKNS-0.01LT (0.343°) is obviously wider than that of  $(020)_O$  peak (with larger Bragg angle) (0.265°). The dispersion between two



**Fig. 2.** The full width at half maximum (FWHM) of (200) diffraction peaks of NKNS-xLT ceramics.

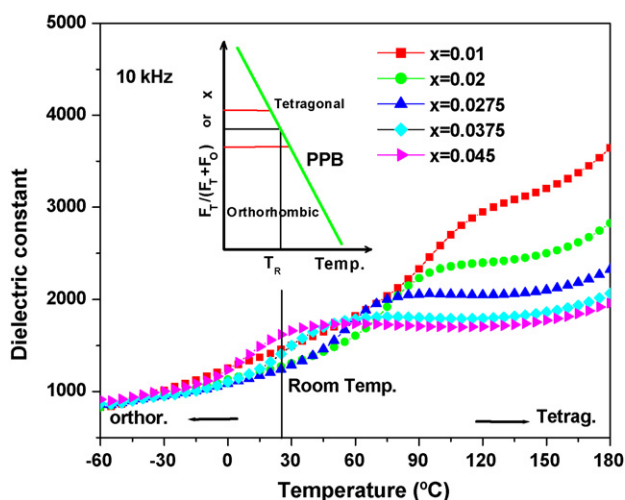


Fig. 3. Dielectric constant at 10 kHz near the polymorphic phase transition as a function of temperature for undoped NKNS-xLT ceramics as indicated.

FWHM values is about  $0.078^\circ$ , indicating that  $(200)_O$  peak is partly overlapped by  $(002)_O$  peak (mainly due to  $a \approx c$ , rather than  $a = c$  for an orthorhombic phase). This dispersion is also partially attributed to the existence of tetragonal phases and gradually increases with increasing  $x$  (or with increasing  $F_T$ ), reaching a maximum value at about  $x = 0.0275$ – $0.0375$  and then decreasing to nearly zero for pure tetragonal phase ( $a = b < c$ ,  $(200)_T$  and  $(020)_T$  completely overlaps such that the FWHM of  $(200)_T/(020)_T$  and  $(002)_T$  peaks is equal). The change of the dispersion with the content of LT implies that there is an orthorhombic–tetragonal coexistence zone near room temperature owing to the change of LT content. On the other hand, the FWHM of diffraction peaks with smaller Bragg angles increases gradually when  $x < 0.0375$ , particularly after  $x = 0.02$ , owing to that the  $(002)_T$  peak is partly overlapped by the  $(002)_O/(200)_O$  peaks, and that the fraction of the tetragonal phase gradually increases. However, it decreases sharply after  $x = 0.045$  probably because the tetragonal/orthorhombic ratio is over a certain value and the effect of peak overlapping becomes weak. For the same reason, the FWHM of diffraction peak with larger Bragg angle exhibits a similar tendency.

A direct observation for an orthorhombic–tetragonal phase transition was made by measuring the dielectric constant of NKNS-xLT ceramics with changing temperature, as shown in Fig. 3. It can be seen that there is a dielectric anomaly owing to the orthorhombic–tetragonal phase transition for all compositions. The location of this dielectric anomaly is gradually shifted downwards with the addition of LT. Another important characteristic is that all these phase transitions are diffuse within a broad temperature range. These observations suggest that the two-phase coexistence states could exist in a wide composition range based on the diffuse nature of phase transition. Accordingly, the respective phase content of orthorhombic and tetragonal phases changes with the variation of composition and temperature, as shown in the inset of Fig. 3. Relative to the composition axis, the boundary line (also called as PPB) between orthorhombic phase zone and tetragonal phase zone forms an acute angle, meaning that electrical properties are very sensitive to temperature and composition as well (two-phase coexistence exists in a wide composition range). Moreover, it can be believed that the diffuse characteristic of orthorhombic–tetragonal phase transition originates from its polymorphism nature that multiple crystals or phases with varying phase transition temperatures coexist. Therefore, PPT behaviors like a relaxor ferroelectric phase transition to a certain degree. If one compares PPB with MPB, an obvious distinction is that the

two ferroelectric phases coexist in an extremely different composition range, far wider for a PPB system. Possible reasons are given below. For a real MPB system (such as PZT), actually there appears “polymorphism” phenomenon which emerges during the period of forming solid solutions between PZ and PT. When the molar ratio of PT and PZ reaches a critical value (near its MPB, PZ/PT = 52/48), one kind of temporary instability in this solid solution system will develop like the phase separation of liquid glasses, and thus lead to the coexistence of two phases. However, this balance can be shortly broken as the ratio of two phases reaches a certain value such that one phase gets stable. During forming solid solutions, the increased internal energy is wasted by temporarily forming two-phase coexistence. That is to say, the phase coexistence in a real MPB system exists in a narrow composition range and therefore the boundary line is nearly vertical to the compositional range (accompanied by good composition and temperature stability). By comparison, for alkaline niobate-based compositions which have a PPT intrinsically, the increased internal energy is consumed not by forming two independent phases (rhombohedral and tetragonal phases for PZT system), but by changing the temperature range of the thermal stability of one of existing phases, such as a downward-shift of PPT. The reason could be that the energy consumed during shifting PPT is much more than that during forming two coexisted phases. The former thus causes the solid solution to have a lower free energy. Noticeably, this is not for all lead-free systems, for example,  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $\text{BaTiO}_3$  system [16] is an exception in which an MPB is formed not by shifting a PPT (rhombohedral ferroelectric phase and tetragonal antiferroelectric phase) to room temperature, but by means of producing two independent phases (rhombohedral and tetragonal ferroelectric phases). From the above discussions, one could find the intrinsic difference between PPB and MPB in terms of the origin and characteristic of these two-phase boundaries.

The piezoelectric constant  $d_{33}$  values are plotted as function of the phase content  $F_T$  and the content of LT  $x$ , as shown in Fig. 4. As we discussed above,  $F_T$  changes from 33.6% to 98.1% as the LT content  $x$  is from 0.01 to 0.045, suggesting that orthorhombic and tetragonal phases could actually coexist in a wider composition range than usually expected. Importantly, the  $d_{33}$  value increases with the addition of LT, reaches its maximum approximately at  $x = 0.0375$  ( $F_T = 65.4\%$ ) and then declines with further increase of  $x$ . The highest  $d_{33}$  value does not appear in the middle of two-phase coexistence zone ( $F_T = 50\%$ ), but close to tetragonal-rich side ( $F_T = 65.4\%$ ). The

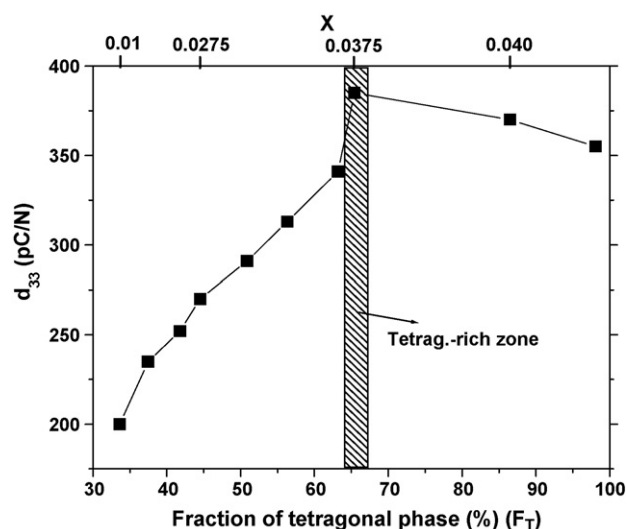


Fig. 4. The variation of  $d_{33}$  values of poled NKNS-xLT ceramics with the LT content  $x$  and the fraction of tetragonal phases  $F_T$ .

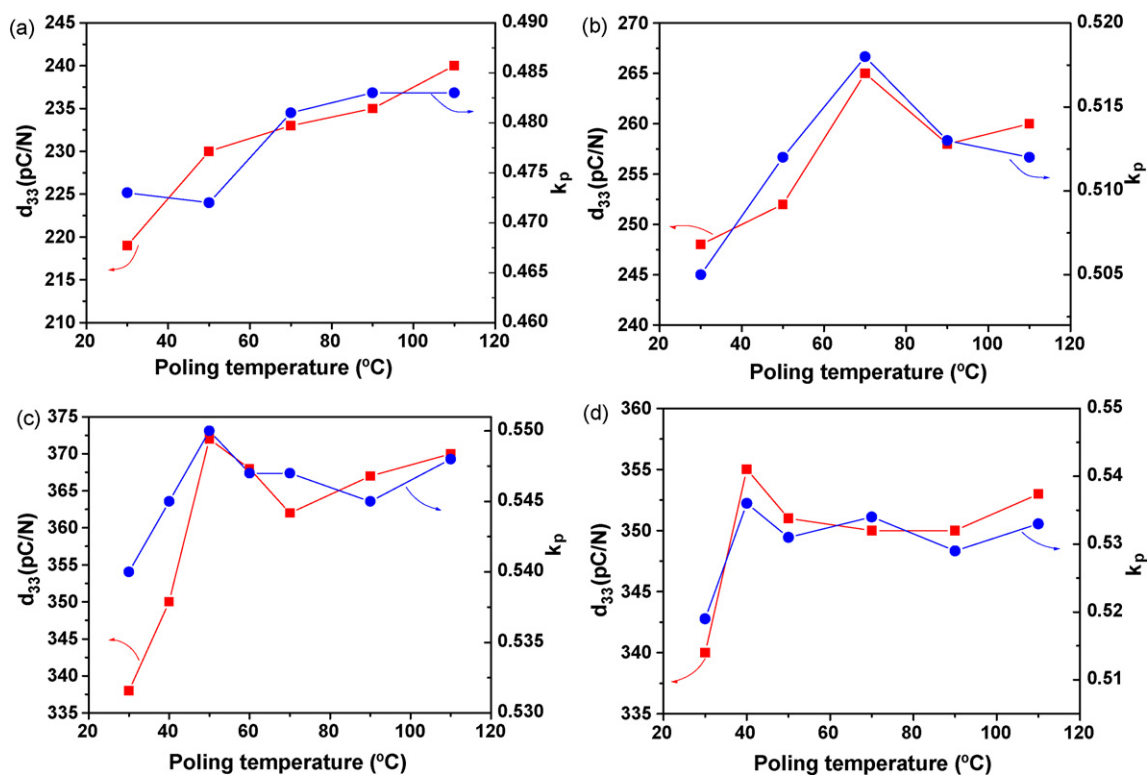


Fig. 5. Both  $d_{33}$  and  $k_p$  values of NKNS-xLT ceramics as a function of poling temperature: (a)  $x=0.02$ , (b)  $x=0.0275$ , (c)  $x=0.0375$  and (d)  $x=0.045$ .

reason for this could be correlated to specific PPT behavior of this system. Because samples for the  $d_{33}$  measurement were poled under a dc field of 3 kV/mm at 110 °C, at which each composition should be composed of different phase contents. For each composition with larger  $x$ , it should consist of more  $F_T$ . Therefore, it should suffer from less influence of tetragonal to orthorhombic phase transition during cooling after high-temperature poling processing. Part of oriented tetragonal domains or polarization vectors would diminish or reorient, leading to a loss of the  $d_{33}$  value. The less the content of orthorhombic phases in the composition, the less the effect owing to the tetragonal to orthorhombic phase transition. However, considering that the two-phase coexistence is a pre-condition of for optimum piezoelectric properties, thus the  $d_{33}$  value should decline over a certain  $F_T$  value.

For the same reason, the NKNS-xLT ceramics exhibit an obvious poling processing dependence, as shown in Fig. 5. Firstly, it can be seen that both  $d_{33}$  and  $k_p$  exhibit maximum values as samples are poled at temperatures closer to the  $T_{o-t}$  of the corresponding compositions. Secondly, the piezoelectric properties of each composition first increase with an increase of poling temperature, reaching a maximum value, then start to decrease with further increase of poling temperature and finally increase again at higher poling temperature. It is understandable that piezoelectric properties are generally enhanced with increasing poling temperature because at higher temperature the domain orientation should be easier under an external electrical field. However, the optimum piezoelectric properties for each composition only appearing at a appropriate poling temperature (near its  $T_{o-t}$  defined as the temperature at maximum dielectric constant within a PPT zone in a dielectric constant versus temperature curve) could be attributed to the existence of PPB for this system, because the two-phase coexistence near PPB make polarization vectors easily switch during poling, compared to the state of a single orthorhombic or tetragonal phase as the poling temperature deviates from  $T_{o-t}$ . Owing to that two-phase coexistence exists within a wide composition or tem-

perature range, piezoelectric properties of alkaline niobate-based PPB systems exhibit remarkable poling temperature dependence. Actually, this kind of specific PPB, rather than a classic MPB has led to a few other physical phenomena, such as thermal instability of piezoelectric properties [10,17,18].

#### 4. Summary

The phase coexistence and the fraction of coexisted phases were semi-quantitatively investigated for typical alkaline niobate-based lead-free piezoelectric compositions. The intrinsic difference between a classical MPB (mostly for conventional Pb-based piezoelectric ceramics) and a PPB (particularly for alkaline niobate-based compositions) was pointed out by taking the diffuse nature of PPT (thus phase coexistence within a broad composition and temperature range) into account. As a result, the optimum piezoelectric properties appear only closer to the tetragonal side and exhibit remarkable poling temperature dependence.

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