Imaging chemical concentration pattern and early stages of spinodal decomposition in the Ag$_x$Na$_{1-x}$Br system by scanning force microscopy

F Güthoff, B Zhang and G Eckold

1 Institut f. Phys. Chemie, Georg-August-Universität Göttingen, D-37077 Göttingen, Germany

2 Forschungszentrum Jülich, Institute of Complex Systems (ICS-1), D-52425 Jülich, Germany

E-mail: fguetho@gwdg.de

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Abstract

In quasi binary systems like AgBr–NaBr the demixing from the homogeneous high temperature phase into separated phases is a complex process that depends on the ageing temperature as well as on the quench rate. Spinodal decomposition and nucleation processes can be distinguished which lead, however, to the same final equilibrium state. Using frequency modulated scanning force microscopy we aimed to distinguish the demixed phases and their morphologies on a nm-scale at room temperature for samples with different concentration. While no contrast between the different phases are observed in the usual topographic mode, a modified evaluation of Kelvin experiments allows the distinction of silver- and sodium enriched phases. Moreover, direct evidence is found for concentration fluctuations which are characteristic for spinodal decomposition.

1. Introduction

Silver alkali halides and, in particular Ag$_x$Na$_{1-x}$Br, provide ideal model systems for the investigation of decomposition mechanisms in quasi-binary solid electrolytes. Different from metallic alloy or polymer systems the phase separation takes place within the almost rigid frame of the halide ions and is entirely limited to the fcc cation sublattice. The simple phase diagram [1] with no structural anomalies makes this system well suited for detailed investigations on the microscopic mechanism.

The kinetics of decomposition of silver–alkali halide mixed single crystals was studied in great detail by means of inelastic and small angle neutron scattering (SANS) experiments in reciprocal space [2–4]. Different annealing temperatures chosen for the quenching process enables the distinction between the metastable nucleation and the unstable spinodal regimes, respectively. Moreover, these results allow the control of the spinodal decomposition process and the corresponding formation of nano-scaled structures.

Due to the fact that silver and alkali halides exhibit extremely different water solubility careful surface etching in the system AgCl–NaCl was done [5] and periodic surface patterns could be observed using SFM under ambient conditions. It was found, that the annealing temperature and duration determine the patterns thus complementing the above mentioned scattering experiments. However, the determination of the nano-scaled composition pattern of as-grown single crystal surfaces without any chemical treatment was hitherto not possible. Therefore, we employed a special spectroscopic technique of frequency modulated scanning force microscopy (FM-SFM) which allows the determination of the local chemical composition.

In the last decades, the progress in different scanning techniques led from ordinary surface scanning to in-depth material studies. As many surfaces refuse atomic resolution at ambient temperatures different approaches like electrostatic force microscopy [6] or scanning capacitance microscopy (SCM) [7], magnetic force microscopy [8] and Kelvin Probe Force microscopy (KPFM) [9] were invented for a variety of materials. Additionally, different tip forms and coatings are frequently used to optimize the analytic investigations. A short compilation of different methods is given by Barth et al [10].
In this paper, we report on measurements where we make use of the ordinary spectroscopic method, by varying the voltage between a standard silicon tip and the surface during the scan process at equidistant positions. We will show that the evaluation of the entire frequency—voltage profile of the tip allows, in fact, the distinction between regions of different chemical composition. In the following this procedure is called ‘static Kelvin method’ in contrast to the more usual KPFM technique.

Due to the complex tip–sample interaction the influences of tip size, oscillation amplitude and working-point for distance controlling are elucidated. In a phenomenological approach, the change of the force component due to different electrical polarizabilities of the Ag-rich and Na-rich phases is expressed.

These investigations were done on single crystalline samples of various compositions Ag\(_{x}\)Na\(_{1-x}\)Br \((x = 0.23, 0.35\) and 0.6\) after different heat treatments leading to characteristic length scales of the demixing pattern as deduced from SANS experiments [3].

2. Experimental

2.1. Crystal growth and preparation

Mixed single crystals of Ag\(_{x}\)Na\(_{1-x}\)Br with different concentrations were grown by the Bridgman technique. In a first step, AgBr and NaBr powders (AgBr (99.9%), NaBr (99.5%) delivered by Alfa and Fluka respectively) with different concentrations were mixed and degassed at 100 °C in high vacuum for several hours. After the first melting process at temperatures around 800 °C the sample surface was mechanically cleaned. The ingot was shredded and filled into quartz ampoules for the growth process. After complete solidification the temperature was lowered either by quenching or by ambient cooling. The homogeneous samples pass the demixing temperature without losing its crystal perfection. The phase separation is driven either by nucleation process or spinodal decomposition depending on the cooling rate. Crystals of appropriate orientations were cut from the boule after characterization with the help of gamma-ray diffraction. The actual concentration was determined from the Bragg intensities corresponding to the product phases at room temperature. To avoid photo reduction the crystals were handled under amber light and wrapped in silver foil when analysed by gamma-ray diffraction.

One Ag\(_{x}\)Na\(_{1-x}\)Br—sample was grown by chance as a strong gradient single crystal. This gave us the opportunity to study regions of different overall concentrations using SFM without changing set-up parameters for regulation and cantilever driving.

Due to the different samples sizes, most of the crystals where fixed on sample plates by gluing. Subsequent cleaving along the (100)–plane with a razor blade was done under dry air condition outside the SFM. This has been done for reasons of simplicity rather to get a perfect surface which lies beyond the scope of the experiments. Also, some crystals were cut by edge bending in the sample preparation chamber under high vacuum. Due to the corrosive activity of the samples all measurements were done at room temperature. Hence, even the initial states of (spinodal) decomposition could be investigated in situ if large quench rates were applied since it is known from SANS experiments [3] that the kinetics of phase separation at room temperature occurs on time scales of several hours and characteristic length scales of the order 10–100 nm can be expected.

2.2. SFM Measurements

The cleaved samples were transferred to the UHV-chamber \((2 \times 10^{-10} \text{ mbar})\) of a commercial SFM-system (Omicron VT). All experiments were done in FM non-contact scanning mode [11]. The tip–sample distance was kept constant by controlling the frequency shift \(f\) between the resonance frequency \(f_0\) and the actual frequency \(f\) of the cantilever. Using n-type silicon tips (NSG10) from NT-MDT typical resonance frequencies \(f_0\) in the order of 200 kHz and spring constants \(k\) of about 16 N m\(^{-1}\) were determined. For regulation purpose \(df\) of 15–25 Hz was used. The scanning speed of the cantilever was depending on the surface roughness. The favourite speed was about 1000 nm s\(^{-1}\) for a grid of 300 × 300 data points. The vibration of the cantilever was driven by a voltage from 0.3 to 1 V which corresponds to amplitudes in the order 4.5 to 15 nm. To compensate the electrostatic potential between tip and sample (PD) the bias voltage \(U_{bias}\), which was determined in static Kelvin-experiments, was applied with respect to the grounded sample.

3. Surface scans for phase characterization from demixed samples

Before starting surface scans in a conventional procedure, the PD is determined on a flat region as the minimum of the force gradient function which depends on the applied bias voltage between tip and sample with distance \(z\). In a simple ansatz for a homogeneous electric field this can be expressed by
and hysteresis artefacts. Important since otherwise the scanning parameter could lay far from optimum which results in bad resolution. This method implies that the species on the surface to be scanned have the same PD. This is particularly given by the binodal in the phase diagram can be assumed. The sample was cleaved on dry air. The photograph in cooled down rather slowly from the melt to room temperature, so demixing up to the equilibrium concentration sodium rich grains with typical dimensions of some 100 nm which is in good agreement with the protrusion pattern. It is likely that the morphological surface structure is due to the presence of silver and the surface colour from greenly to a more yellow colour tone. Moreover, the rough surface reveals a macroscopic detailed SANS experiments. The same results were obtained.

The binary phase diagram of the AgBr–NaBr system [1] shows, that the demixed phases contain a maximum of only 8% cations of the opposite compound at ambient temperature. Within the rigid frame of halide ions the different cation species are randomly distributed. In combination with the low lateral resolution of 2–6 nm it is therefore impossible to resolve any potential difference between Ag⁺ and Na⁺-enriched regions. This is in accordance with our finding that the PD-scan does not change considerably when taking it at different position across the scan range.

In figure 1(a) a topological scan across the (100)-surface of a Ag₉Na₁₋ₓBr-crystal is shown. The sample was cooled down rather slowly from the melt to room temperature, so demixing up to the equilibrium concentration given by the binodal in the phase diagram can be assumed. The sample was cleaved on dry air. The photograph in figure 1(b) demonstrates that this sample exhibits a strong concentration gradient as reflected by the variation of the surface colour from greenly to a more yellow colour tone. Moreover, the rough surface reveals a macroscopic protrusion pattern. It is likely that the morphological surface structure is due to the presence of silver and sodium rich grains with typical dimensions of some 100 nm which is in good agreement with the findings of very detailed SANS experiments [2, 3].

Using the SFM in the static Kelvin mode we tried to map the $U_{PD}$ across the surface. This spectroscopic method was realized by interrupting the scan at equidistant scan points and recording the $\Delta f(U_{PD})$-profile which yields $U_{PD}$ as the vertex of the parabola according to eq. (1). As one could see from figure 1(c) no significant variation of the $U_{PD}$ could be detected. There is neither any correlation of the $U_{PD}$ data with the surface structure except for sharp kinks nor any hint for a contrast due to phase separation. Even if the continuous dynamic Kelvin spectroscopy [9] was applied which exhibits improved spatial resolution almost the same results were obtained.

\[
\Delta f \propto \frac{\partial F}{\partial \Delta z} = -\frac{a}{2} \cdot (U_{bias} - U_{PD})^2
\]

with

\[
a = \frac{\partial^2 C}{\partial \Delta z^2},
\]

where $C$ is the capacity between tip and sample. In the following we define $a$ as curvature at the parabola vertex. This method implies that the species on the surface to be scanned have the same PD. This is particularly important since otherwise the scanning parameter could lay far from optimum which results in bad resolution and hysteresis artefacts.

There is a wide spread of factors which enters in $U_{PD}$. In metals, the local work function describes the ability to extract an electron from the surface which is highly material dependent. Also surface contamination like oxide layers, impurities and doping [12] contribute. The reason for the PD in insulating material like the Ag₉Na₁₋ₓBr is the existence of local charges and dipole interaction. The electrostatic charge is strongly influenced by the cleavage structure and surface damage [13]. Due to the ragged surfaces that are obtained after cleaving with an overall roughness about 60 nm, we are not going to investigate these effects in detail.

The measurement of PD should be performed with the sample cooled to room temperature. This was achieved by placing the sample holder in a dry box and quickly changing the sample holder to the microscope. The set up should be stable at the position of the microscope. The sample was scanned in a grid of 60 equidistant scan points. $U_{bias}$ was between 5 V and 3 V in 15 steps. The colour contrast only shows qualitatively the change of the PD at kinks. The PD-distribution over the scanned surface is Gaussian shaped with FWHM of 0.28 V.

**Figure 1.** (a) Scan on a (100) surface from a demixed AgNaBr crystal with a strong concentration gradient. Cleaving was done on dry air. The surface roughness $\Delta z$ is about 90 nm. Scan parameter: $\Delta f = -26$ Hz, $A_{iso} = 0.1$ V, $U_{bias} = -0.2$ V, $raster = 300 \times 300$, 8.3% feedback, $v_{scan} = 1000$ nm s⁻¹. (b) The photograph shows the sample glued with a silver conductive adhesive. The bright colour corresponds to a large overall Na concentration whereas the dark colour reflects the enrichment of silver in the gradient crystal. (c) Measured PD over the surface with a grid of 60 × 60 equidistant scan points. $U_{bias} = -5$ V to 3 V in 15 steps. The colour contrast only shows qualitatively the change of the PD at kinks. The PD-distribution over the scanned surface is Gaussian shaped with FWHM of 0.28 V.
The advantage of static Kelvin method is that it does not only provide information about $U_{PD}$ but also about the form of the vertex parabola as described by equation (1). In particular, the curvature $a$ depends on the polarizability of the sample area below the FM-tip and, hence, on the chemical composition. It is worthwhile to mention that in contrast to dynamic SCM where the first derivative of $C$ or $C$ itself is determined by local rf-impedance measurements, the curvature $a$ (equation (2)) as the second derivative of $C$ is measured in a quasi-static setup. This curvature is obtained by a least squares fit of the $\Delta f(U_{bias})$ data as shown in figure 2 (middle column). The parameter $a$ obtained at the grid points is plotted across the scan area. A clear contrast is observed which varies with the average concentration of the sample. To study the origin of this contrast, we scrutinized $a$ for its physical origin. For a spherical cone, the contributions of Coulomb- and van der Waals-interaction (vdW) to the force gradient can be written as

$$\Delta f_c = -\frac{\pi f_0 \varepsilon_0 R_0}{kA^{3/2}\sqrt{2d}} \cdot \left(U_{bias} - U_{PD}\right)^2$$

and

$$\Delta f_{vdW} = -\frac{f_0 A_H R_0}{12 \sqrt{2} kA^{3/2}d^{3/2}}.$$

respectively [14–16], where $\varepsilon_0$ denotes the vacuum permittivity, $R_0$ the radius of the tip apex, $k$ the spring constant, $A$ the tip oscillation amplitude, $d$ the tip–sample distance and $A_H$ the Hamaker constant [17]. Different from long range electrostatic forces of single charges on surfaces or surface imperfections, calculations for electrostatic imaging on ideal ionic KBr crystals [18] demonstrated, that the magnitude of the electrostatic field decays exponentially. This behaviour is similar to what is expected for vdW-forces. Hence, both interactions contribute to the total force which is the control parameter for SFM regulation. As for static Kelvin

Figure 2. Topographic scans (left, 3D-view) show the roughness of different phase contributions after demixing, curvature $a$ of the parabola from spectroscopic measurements (middle) and the histogram of the contrast evaluation (right) on three different positions on a gradient Ag, Na$_{0.3-\epsilon}$Br sample. The dark regions of the Kelvin experiment correspond to the Ag rich phase, the bright regions to the Na rich phase. The scan width is 1500 nm, the scale in z-direction about 100 nm. The normalization of density $\rho$ in the histograms is given by $\int \rho(a) \, da = 1$. 

(a) NaBr enriched part

(b) balanced concentration of AgBr and NaBr

(c) AgBr enriched part
measurements $\Delta f_{\text{relv}}$ is independent of the applied voltage (equation (3)) and the curvature of the vertex parabola is simply given by:

$$a = -2\frac{\pi f_0 \varepsilon_0 R_0}{kA^{3/2} \sqrt{2d}}.$$  

For an insulating material, the prefactor has to be modified since the polarizability of the sample needs to be considered. The bulk properties are taken into account by the relative permittivity $\varepsilon$. The two components of a demixed Ag$_x$Na$_{1-x}$Br sample exhibit permittivities which differ by a factor of about 1.5 [19]. Since the thickness of the samples is always much larger than typical grain sizes, the effective bulk permittivity turns out to be an average value and does not induce any spatial variation of the capacity. At the free surface, however, the local electric field is enhanced leading to an excess surface polarization [20] which is different for Na-rich and Ag-rich regions. Therefore, the force gradient acting on the SFM-tip does indeed depend on the local concentration $x$ of the sample. In general, we can formulate this result in the following form for the curvature $a$:

$$a_{\text{insulator}} = -2\frac{\pi f_0 \varepsilon_0 R_0}{kA^{3/2} \sqrt{2d}} \cdot \varepsilon \cdot f(P),$$  

where $f(P)$ is some function of the surface polarization $P$. Obviously, $P$ depends on both, the tip–sample distance $d$ and the local concentration $x$. With the separating ansatz

$$P(d, x) = R(d) \cdot S(x).$$  

we can now factorize $a_{\text{insulator}}$ to yield:

$$a_{\text{insulator}} = C_0 \cdot T \cdot G(A, d) \cdot M(x)$$  

with

$$C_0 = -\sqrt{2} \pi \varepsilon_0 = \text{const}$$  

$$T = -\frac{f_0 R_0}{k}$$  

which depends on the tip parameters only,

$$G(A, d) = \frac{R(d)}{A^{3/2} \sqrt{d}}$$  

which depends on the operational parameters of the SFM scan only, and

$$M(x) = S(x) \cdot \varepsilon$$  

for characterising the sample with its varying surface concentration $x$.

During the experiments even on different sample positions (see figure 1(b)) most of the parameters entering in the expression for $a$ are constant. Different values of the $a_{\text{insulator}}$ obtained in a static Kelvin experiment thus provide information about the variation of the surface concentration and the size of precipitates which are formed during demixing. Figure 2 shows typical results for three different positions on a large single crystal with different concentrations. Higher (bright) while the middle column shows the variation of the parameter $a_{\text{insulator}}$. Obviously, there are well defined regions with high (dark) and small (bright) values of $a_{\text{insulator}}$ which can be identified as the two demixed phases with different concentrations. Higher (smaller) values of $a_{\text{insulator}}$ correspond to the silver (sodium)-rich phase. It is also seen that the topological structure is hardly related to the formation of these silver-rich and sodium-rich precipitates.

The probability distribution $h(a)$ of $a_{\text{insulator}}$-values is given by the histogram plots on the right hand side of figure 2. Note, that a logarithmic scale is used on the absissa. There is a clear two-peak structure which corresponds to the well separated concentrations of the precipitates. The relative intensities of both peaks directly reflect the overall concentration $x$ of the Ag$_x$Na$_{1-x}$Br sample across the scanned region which increases from top to bottom of this figure for this particular gradient sample. For a ragged surface, there is an apparent variation of the effective tip-to-sample distance and consequently of the function $G(A, d)$ (equation (10)). In the logarithmic representation of $a_{\text{insulator}}$

$$\log a_{\text{insulator}} = \log C_0 + \log T + \log G(A, d) + \log M(x)$$  

this leads to an additive contribution and, hence, to a broadening of the probability distribution $h(\log(a))$. The widths of the two peaks in the histograms in figure 2 (right column) are therefore essentially determined by the surface roughness. The finding that the larger value of $a_{\text{insulator}}$ corresponds to the silver rich phase agrees with the observation that silver ions with the electron configuration $[\text{Kr}]4d10\ 5s1$ exhibit larger polarizabilities than sodium ions [21]. As a result, the induced dipole interaction leads to stronger force gradients above silver rich grains.
Figure 3(a) shows a topographic scan sequence on a silver rich phase, where the cantilever scans from left to right operating in the static Kelvin method. The cantilever stops every 5th scan point at every 5th scan line and varies the bias voltage from $-4$ to $+4$ V in between 12 steps. These particular scan lines show ridges with an apparent height of about 0.6 nm. The backward scans as shown in figure 3(b) are standard topographic scans. At the beginning of these backward scans on the right hand side, there are some residues of the ridges visible that have been generated during the preceding Kelvin-mode scan. Obviously, the perturbation by Kelvin spectroscopy persists on a time scale which is comparable to the scan duration. From the scanning parameter (including the spectroscopy points and scanner delay times) one can estimate characteristic relaxation times of roughly 0.3 s. In the case of sodium rich surface areas, this disturbance was scarcely measured.

Similar observations have been obtained from a CaF$_2$-crystal by Bennewitz et al.\textsuperscript{[22]} after irradiation with slow electrons. In that case, relaxation time could be related to the ionic conductivity by the relation

$$\tau = \frac{\varepsilon \sigma}{D},$$

Interestingly, this relaxation time of about 50 s is much smaller than a characteristic residence time for ionic hopping diffusion (about 1000 s) as estimated from the diffusion coefficient or conductivity and structural parameters of CaF$_2$. In the present case of AgBr, the ionic mobility is about six orders of magnitude larger yielding a characteristic time of the order $\tau_{\text{calc}} \approx 50 \mu$s. This is, however, almost four orders of magnitude smaller than the observed relaxation time of $\tau_{\text{exp}} \approx 0.3$ s indicating that the basic mechanism in AgBr is entirely different to CaF$_2$.

Moreover, the residence time for jump diffusion of silver ions at ambient temperature is of the order of $10^{-3}$ s. Hence, we believe that the observed field induced surface effects might be due to a collective rearrangement of silver ions with the occupation of interstitial sites according to the Frenkel type of disorder. This would be associated with the formation of space charges similar to what Granzer et al have been discussed in [23]. Due to the relative large distance between tip and sample of several 10 nm, a considerable number of silver ions is affected by the strong electric field and may lead to a silver terminated surface when the tip is negatively charged.

The apparent height of the ridges in figure 3(a) is found to be of the order of one lattice constant. This effect can hardly be described by the growth of an additional layer as the relaxation is continuous and the height itself depends on the cantilever amplitude: the smaller the amplitude the larger are the ridges. This finding is due to the fact that the average force acting on the tip would become smaller when the oscillation amplitude is reduced at constant distance. Hence, the SEM control system automatically moves the cantilever towards the sample in order to restore the average force. This leads to an increased electric field when a voltage is applied to the tip and, hence to the observed enhancement of the surface modification.

Almost no such effects have been observed if the static Kelvin method was applied on sodium-rich regions of the demixed crystal. This is not surprising since sodium ions exhibit a mobility which is by two orders of magnitude smaller than that of silver ions and they are diffusing via the vacancy rather than the interstitial mechanism.
4. Evidence for first stages of spinodal decomposition on a quenched Ag$_{40}$Na$_{60}$Br-sample

While the previous results have been obtained using a fully demixed sample which yields large grains of silver-rich and sodium-rich phases, we have also studied the early stages of spinodal decomposition after quenching deep into the miscibility gap. It is known from small angle and elastic neutron scattering that concentration fluctuations at constant lattice parameter govern the short time behaviour while the adaptation of the equilibrium structure and the release of coherency strains occur on much larger time scales. The kinetics was shown to vary drastically with the annealing temperature. At room temperature, e.g., the growth of concentration fluctuation needs hours while the coarsening and the formation of large grains is observed only after several days or weeks.

Since in situ experiments at elevated temperature cannot be performed under high vacuum due to the considerable vapour pressure of AgBr, we quenched single crystals from the homogeneous phase at about 350 °C to room temperature ex situ within about 10 s. Subsequently, they are transferred into the preparation chamber of the SFM for cleaving. Thus, the first data were taken few hours after the quench. It should be noted that the roughness of the cleavage planes was much smaller than that of the two-phase demixed systems described above and resemble those which are usually found in simple salts. This is a clear indication that the samples were still homogeneous after the quench which is also confirmed by the fact that the static Kelvin spectroscopy did not yield any phase contrast. Only some surface contours like cleavage edges are seen. Repeated scanning across a selected flat surface region yield, however, that protrusions are created and sometimes also destroyed as shown in figure 4: in an early stage (figure 4(a)) only two protrusions are observed in the scanned region. Their apparent height is similar to the terrace on the right hand side which is of the order of one lattice constant (0.6 nm) and its diameter is found to be about 10 nm. After a while, almost the entire surface is decorated with new protrusions of comparable sizes. The formation of this regular pattern cannot be explained by contamination losses from the tip. Moreover, the stable contour of the cleavage edge also excludes the separation of particles from kinks or steps.

We therefore argue that these structures reflect regions of different forces acting on the SFM-tip which are converted into an apparent height profile just as having been observed during the relaxation processes as described in the previous section. Different from electric field induced surface modifications, here concentration fluctuations being characteristic for the early stages of spinodal decomposition seem to be responsible for the
unusual SFM-pattern. While at the beginning single fluctuations lead to isolated clusters, a more or less regular pattern is formed subsequently just as expected from the Cahn–Hilliard theory of spinodal decomposition. The size of the protrusions and their distance are in good agreement with the results from SANS which yield a characteristic wavelength of the critical concentration fluctuation of about 20 nm [3]. It must be noted, however, that the demixing process at the surface might differ from the bulk. On the other hand, earlier SFM-data on etched surfaces of demixed AgCl–NaCl crystals with limited resolutions [5] provide evidence that processes at surfaces are well correlated with bulk data.

The interpretation of the SFM-patterns of figure 4 by concentration fluctuations is confirmed by the observation of the creation as well as annihilation of such structures during a scan. In figure 5, it is clearly seen that only half of a typical protrusion is mapped. The corresponding profiles of two subsequent scan lines show that the new structure is created in between. In other cases it has also been observed that some fluctuations are being destroyed.

5. Conclusions

In the article we demonstrate FM-SFM measurements on AgNaBr-crystals at room temperature. The samples were differently treated after the growth process. When lowering the temperature quite slowly, the crystals demix and the corresponding grains could be distinguished by the morphology of the surface roughness. The actual concentrations of the two phases is, however, not accessible by conventional SFM methods.

Therefore we used an extended evaluation of the static Kelvin experiment, where we focused on the curvature of the Kelvin-parabola. This parameter shows a strong contrast over the surface of the demixed sample. The origin of the contrast was associated in a simple ansatz with the differences in polarizability of the majority phases. To the best of our knowledge, this is the first application of this method for the determination of local concentrations on a mesoscopic length scale.

When quenching the crystals to room temperature, the demixing process is sluggish enough to allow in situ investigation within the time scale of SFM scans. Concentration fluctuations on a flat surface region during spinodal decomposition could, in fact, be detected and mapped in direct space. These findings complement results from time-resolved neutron scattering and access even the early stages where Cahn–Hilliard theory is applicable.

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