Tuning the optical isotropic point of mixed crystals of ethylenediammonium sulfate/selenate

Melissa Tan, Alexander T. Martin, Alexander G. Shtukenberg and Bart Kahr*

Department of Chemistry, New York University, New York, NY 10003, USA. *Correspondence e-mail: bart.kahr@nyu.edu

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In anisotropic crystals, optical isotropic points are wavelengths where linear birefringence disappears because the refractive indices for both eigenmodes are accidentally equivalent. Here, the optical isotropic point of ethylenediammonium selenate (EDSe) is tuned by generating a solid-solution series of EDSe doped with sulfate. Mueller matrix polarimetry and single-crystal X-ray diffraction are used to correlate changes in linear birefringence with the crystal composition of $\text{EDS}_x\text{Se}_{1-x}$. A scheme for using mixed crystals with isotropic points as tunable birefringent optical bandpass filters is proposed and their performance is modeled.

1. Introduction

The functions of optical devices, including filters, frequency converters, displays and switches, can be expanded by tuning the optical properties of constituent crystals. Crystal properties can be controlled by modulating the growth environment (*e.g.* temperature, external pressure, electromagnetic field, ambient medium) or by altering the physical properties of the crystal itself (*e.g.* thickness, orientation, surface roughness, shape, and bulk or surface impurities) (Billings, 1949; Hips & Crosby, 1979; Dmitriev *et al.*, 1999; Sumioka *et al.*, 2002; Kato, 1994; Jaffe *et al.*, 2016; Glazer *et al.*, 2012; Huband *et al.*, 2017*a,b*). In this work, we present a solid-solution series composed of crystals with a tunable isotropic point, and variable optical activity, based on the quantity of isomorphous anion additives in the host.

Ethylenediammonium is a flexible cation that has been characterized in salts of more than 40 anions, many of which are isostructural and some of which are isomorphous with one another (Srinivasan *et al.*, 2013). Recent research has employed Mueller matrix polarimetry with variable coherence optical models (Postava *et al.*, 2002; Nichols *et al.*, 2015; Martin *et al.*, 2017*b*; Nichols, 2018; Arteaga & Kahr, 2019) to establish the linear birefringence (LB) and circular birefringence (CB) anisotropies in isomorphous crystals [space groups $P4_{1(3)}2_12$] of ethylenediammonium sulfate (EDS) (Nichols *et al.*, 2016) and ethylenediammonium selenate (EDSe) (Martin *et al.*, 2017*a*). These isomorphs differ in the near-visible part of the electromagnetic spectrum in that EDSe exhibits an isotropic point, an accidental linear anisotropy compensation (Hobden, 1968*a,b*), and EDS does not. EDSe, formally uniaxial, is effectively isotropic at 364 nm. Mixed crystals ($\text{EDS}_x\text{Se}_{1-x}$) are easily grown by evaporation from aqueous solutions. Mixed crystals display anomalous biaxiality, a consequence of growth desymmetrization, the selective occupancy of anion sites by additives (Kahr & McBride, 1992; Shtukenberg *et al.*, 2001; Shtukenberg & Punin, 2007).

In contrast with low-symmetry prismatic facets, the {001} growth sectors are associated with surfaces that preserve the fourfold symmetry of the end members in the series, EDS and EDSe. Thus, the ratio of sulfate to selenate in these sub-volumes is statistical and only dependent on the solution composition. As such, the {001} growth sector remains approximately uniaxial with intermediate optical properties determined by the relative ratio of sulfate to selenate.

Here, we use Mueller matrix polarimetry to measure the optical properties of the {001} growth sectors of a series of $\text{EDS}_x\text{Se}_{1-x}$ mixed crystals, and establish the relationship between the site-occupancy factor and the optical properties. The refractive indices are correlated to structure by single-crystal X-ray diffraction, yielding a full structure–property characterization of the series, including a demonstration of isotropic point shifts with composition.

Does this control over the isotropic point have a function? We explore the use of mixed crystals with isotropic points in optical devices. In the 1980s, Yeh designed a class of bandpass filters whose operating principle was based on the isotropic point of a pure crystal (Yeh, 1980, 1981, 1985). Here, we extend that design to mixed crystals, proposing a system of devices with a tunable transmission spectrum dependent on the relative anion concentration. One other mixed crystal system that could be used in such a device is $\text{LiNb}_{0.94}\text{Ta}_{0.06}\text{O}_3$, which exhibits an isotropic point at 632.8 nm at room temperature (Wood *et al.*, 2008). Other pure crystals with isotropic points at accessible optical frequencies may also be candidates, provided high-quality mixed crystals can be grown.

Additionally, researchers have identified several advantages of crystals with isotropic points as temperature probes (Romanyuk & Romanyuk, 2005; Glazer *et al.*, 2011), including high-temperature resolution, protection from electromagnetic interference and stability with temperature cycling. Moreover, such crystals have a built-in temperature reference. Mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$ with tunable isotropic wavelengths are easy to grow from aqueous solution, are inexpensive, exhibit excellent optical clarity and cleave well along {001}, making them potential candidates for use in optical filters or for optical thermometry.

2. Experimental

2.1. Crystal growth, morphology and optical heterogeneity

EDS and EDSe were synthesized as described previously (Cheung *et al.*, 2008; Martin *et al.*, 2017a), and mixed crystals ($\text{EDS}_x\text{Se}_{1-x}$) were grown from saturated aqueous solutions at room temperature, with the exception of Sample *E* which was grown at 413 K. The solubility of EDS in deionized water is ca 0.5 g ml^{-1} at 296 K, while that of EDSe is closer to 1.2 g ml^{-1} . Solutions composed of 50 mol% EDS and 50 mol% EDSe yielded a crystal composition of $\text{EDS}_{0.98}\text{Se}_{0.02}$, as determined by single-crystal X-ray diffraction. A 1:1 ratio of sulfate to selenate in the solid state was achieved from solutions containing 20 mol% EDS to 80 mol% EDSe. Mixed crystals of EDS and EDSe can be cleaved with a razor blade by applying

Figure 1

Mixed crystals of EDSe ($\text{EDS}_x\text{Se}_{1-x}$) grow with dominant {111} and {112} prismatic faces. In general, {101} and {102} faces are expressed to a lesser extent. Thin sections are easily obtained by applying even pressure normal to [001]. The pattern of anomalous birefringence displayed in slices evolves with the height of the biprism. The second and third rows of images display thin sections obtained from crystals of $\text{EDS}_x\text{Se}_{1-x}$ with different compositions. The images on the left were taken between crossed polarizers, while those on the right were obtained with the addition of a first-order waveplate. The anomalous biaxiality in the lateral growth sectors is modest, a consequence of the substitution of tetrahedral anions for one another. As the crystal composition approaches 1:1 sulfate:selenate, the birefringence increases, as displayed in the third row of images. Scale bars are 100 μm .

even pressure perpendicular to [001]. Fig. 1 displays optical images acquired between crossed polarizers, showing growth-sector-specific birefringence. Distinctions between the prismatic and basal sectors are enhanced with a first-order red waveplate.

2.2. X-ray diffraction

Single-crystal X-ray diffraction experiments were conducted with a Bruker SMART APEXII CCD diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Temperature control was maintained using an Oxford Cryosystems 700+ cooler. In order to determine the concentration of sulfate to selenate in {001} growth sectors, a small fragment was excised from the basal sector while viewing the crystal between crossed polarizers. Samples were mounted on a 200 μm loop (MiTeGen) with Type B immersion

oil (Cargille Laboratories). Data processing, including unit-cell determination, data reduction and absorption correction, was completed using the Bruker *APEX2* software suite (Version 2013.12; Bruker, 2012). The structure was refined by a full-matrix least-squares method on F^2 in *SHELXL* (Sheldrick, 2008, 2015). Non-hydrogen atoms were refined with anisotropic displacement parameters, while hydrogen atoms were placed at calculated positions and refined with a riding model. The site-occupancy factors of sulfate and selenate were refined with the PART instruction, and the positional and displacement parameters of sulfur and selenium were constrained by EXYZ and EADP. The absolute configuration was determined from the Flack parameter (Flack & Bernardinelli, 1999) and confirmed with a petrographic microscope (Matsumoto *et al.*, 2015).

2.3. Mueller matrix polarimetry

Mueller matrix spectra were acquired with a home-built polarimeter that operates four photoelastic modulators to simultaneously recover the complete Mueller matrix. The Mueller matrices of the {001} growth sectors of eight mixed crystals of various compositions were measured for a range of angles of incidence (AOIs) from -30 to 30° in 10° intervals and for wavelengths ranging from 300 to 750 nm in 1 nm intervals. Measured spectra (Fig. 2) were analytically inverted (Arteaga & Canillas, 2010) to the linear retardance (LR) and subsequently fitted to optical dispersion relations for ϵ using nonlinear fitting algorithms in MATLAB.

3. Results and discussion

Both EDS and EDSe belong to the tetragonal enantiomorphous space groups $P4_{1(3)}2_12$. At 100 K, the unit-cell parameters of EDS are $a = 5.9762(4)$ Å and $c = 17.986(2)$ Å, while those of EDSe are $a = 6.1155(4)$ Å and $c = 18.132(1)$ Å. Data collected from the {001} growth sector of a series of mixed crystals indicate a linear correlation between the unit-cell parameters and the concentration of selenate in the crystal, obeying Vegard's rule (Crundwell *et al.*, 1999; Gopalan & Kahr, 1993). In all refinements, the % R factor improved by accounting for substitutional disorder between anions.

3.1. Mueller matrix polarimetry

Recent developments in the field of Mueller matrix polarimetry, including polarimeter design (Arteaga *et al.*, 2012), optical modeling (Nichols *et al.*, 2017) and data fitting (Martin, 2018), have greatly improved our ability to measure dispersion in optical tensors of bianisotropic media. The partial wave method (Nichols *et al.*, 2015) was employed here to calculate the Mueller matrix, a 4×4 polarization transformation matrix that encodes all information related to the linear optical effects: LB, CB, linear dichroism (LD) and circular dichroism (CD). The partial wave method accounts for loss of coherence between multiple reflections or multiply reflected transmissions in ellipsometry and polarimetry, respectively. Calculating the Mueller matrix requires the Tellegen optical constitutive tensors (Mackay, 2010) which define refraction, reflection, polarization transformation and

Figure 2

Measured Mueller matrix spectra of the {001} growth sector of a 420 μm thick c -cut mixed crystal of $\text{EDS}_{0.46}\text{Se}_{0.54}$ (Sample *E*) from 300 to 750 nm for four angles of incidence: 0° (green), 10° (purple), 20° (red) and 30° (blue).

absorption for a given material based on electronic structural symmetry. In addition, the model requires knowledge of extrinsic material properties, such as thickness, surface roughness and crystallographic orientation, as well as instrument properties like the coherence volume of the light source.

The constitutive optical tensors for the {001} growth sector of $\text{EDS}_x\text{Se}_{1-x}$ have approximately the same symmetry as for pure EDS or EDSe, given by

$$\epsilon = \text{diag}(\epsilon_{11}, \epsilon_{11}, \epsilon_{33}), \quad (1a)$$

$$\alpha = \text{diag}(\alpha_{11}, \alpha_{11}, \alpha_{33}), \quad (1b)$$

$$\mu = \mathbf{I}, \quad (1c)$$

relative to the crystallographic optic axis, where ϵ is the dielectric permittivity, α is the magnetoelectric tensor, μ is the permeability and $\mathbf{I}$ is the 3×3 identity matrix.

Fig. 3 depicts the measured LR spectra for two mixed crystals (colored by AOI, where green = 0° , purple = 10° , red =

Figure 3

Polarimetric measurements of the {001} growth sector of two *c*-cut mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$, analytically inverted from the Mueller matrix to linear retardance (LR). (Top) LR spectra collected from a 355 μm thick crystal (Sample *A*, $\text{EDS}_{0.18}\text{Se}_{0.82}$) from 300 to 750 nm for seven angles of incidence: 0° (solid green), 10° (solid purple), 20° (solid red), 30° (solid blue), -10° (dashed purple), -20° (dashed red) and -30° (dashed blue), overlaid in black with the fitted spectra. The isotropic wavelength is highlighted by an arrow. (Bottom) LR spectra collected from a 420 μm thick crystal (Sample *E*, $\text{EDS}_{0.5}\text{Se}_{0.5}$) from 300 to 750 nm for the same seven angles of incidence, overlaid in black with the fitted spectra. For uniaxial samples, the sets of measurements with the same magnitude of the AOI (e.g. -30° and 30° tilts from [001]) are commensurate. The furthest deviations from uniaxial optical symmetry occurred when the selenate to sulfate ratio was near parity.

Table 1

Anion fractions of eight mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$.

Sample	Thickness (μm)	Polarimetry		XRD	
		[S]/[S]+[Se], mol% in solution	Fraction SO_4	R^2	Fraction SO_4
<i>A</i>	355	6	0.14	0.9994	0.18
<i>B</i>	388	6	0.15	0.9943	0.19
<i>C</i>	431	6	0.16	0.9494	0.14
<i>D</i>	257	9	0.19	0.9798	0.19
<i>E</i>	420	16	0.46	0.9816	0.50
<i>F</i>	516	18	0.53†	0.9546	0.48
<i>G</i>	357	43	0.64	0.9970	0.618
<i>H</i>	350	49	0.96	0.9967	0.988

† Maximum AOI measured = $\pm 25^\circ$.

20° and blue = 30°) overlaid with the calculated spectra resulting from fitting to an optical model (black). Note that the optical symmetry of Sample *E* is slightly perturbed from a uniaxial material, as shown clearly by the 0° measurement (green) which does not exhibit null LR even with careful alignment of the beam normal to the {001} cleavage plane. Still, the LR spectra shown in Fig. 3 were reasonably well fitted (Sample *A*, $R^2 = 0.9994$; Sample *E*, $R^2 = 0.9816$) to a simple optical model with only one fitting parameter (the anion fraction x) as a linear combination of ϵ components of pure EDS and EDSe,

$$\epsilon_{ii}(\lambda) = x\epsilon_{ii}^{\text{EDS}}(\lambda) + (1-x)\epsilon_{ii}^{\text{EDSe}}(\lambda). \quad (2)$$

where the tensor values for the pure crystals were taken from the literature (Nichols *et al.*, 2016; Martin *et al.*, 2017a). Fitted parameters for the eight mixed crystals are outlined in Table 1, along with the corresponding R^2 values which ranged from 0.949 to 0.999. Using the fitted dispersion relations, the maximum LB for each mixed crystal was calculated according to

$$\text{LB}_\perp(\lambda) = (\epsilon_{33})^{1/2} - (\epsilon_{11})^{1/2}, \quad (3)$$

representing the LB for all directions contained in the xy crystallographic plane. The magnitude of optical rotation (OR) was calculated by taking the analytic inversion of the Mueller matrix measured for each sample along the optic axis yielding CB, where $\text{OR} = \text{CB}/2$. Fig. 4 shows the optical property transition area across the parameter space spanning wavelength and anion ratio.

While pure EDS and EDSe have distinct LB spectra (including the consequential isotropic point in EDSe) they exhibit similar OR along [001]. The measured OR for Sample *E* was lower than anticipated on the basis of the sample's composition (46% sulfate from fitting the LR). Moreover, although the spectra of Samples *A*, *B*, *C* and *D* are grouped closely around the calculated curve for pure EDSe, they are out of the expected order (see inset panel at the bottom of Fig. 4). Due to these discrepancies, we do not present fitted dispersion relations for the OR tensor here. They may be best modeled by a linear combination of the constitutive tensors for the pure crystalline media where point *E* is an outlier, or there might be some systematic effects not yet considered.

Figure 4

Optical properties of mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$. (Top) LB spectra perpendicular to the optic axis, calculated using the fitted dispersion relations for pure EDS and pure EDSe, and for six of the fitted intermediate mixed crystals, with sulfate percentages labeled. (Bottom) The magnitudes of the OR spectra calculated along [001] for pure EDS (red) and pure EDSe (purple), and measured for four of the intermediate mixed crystals (Sample A blue, Sample C cyan, Sample E green and Sample G yellow). The inset panel shows the measured OR along [001] at 300 nm for all eight experimental samples versus the fractions of sulfate fitted from the LB measurements, with the black curve showing a smooth linear interpolation of OR.

Discrepancies between OR and LB determination may be caused by a perturbation from the uniaxial electronic structure that requires constitutive tensors with lower symmetry to reconcile, or from slight inhomogeneities in the optical properties within the {001} growth sector that are sampled selectively upon tilting the crystal.

In contrast with the OR, the LB of the mixed crystals was easily fitted to the linear combination of refractive index values for the two constitutive crystal structures. Moreover, the calculated fraction of sulfate is correlated with the results from X-ray diffraction. From these data, we can predict the dependence of the isotropic wavelength on the relative anion fractions in the spectral region from 300 to 364 nm, guiding the design of a tunable series of mixed crystals [Fig. 5(b)].

3.2. Tunable optical filters

Optical filters are commonly used to isolate spectral windows in broadband light sources. Birefringent optical filters rely on variable intensity transmission of different polarization states, which can be a consequence of either

polarization-dependent absorption or polarization transformation. As far back as the 1930s, researchers developed various bandpass filter designs based on a series of birefringent crystals, including the Lyot (1933, 1944) and Solc (1965) filters. Both designs require multiple polarizers and anisotropic crystals perpendicular to the optic axis. In the 1980s, Yeh discovered a simpler design, which requires only one birefringent crystal, though an isotropic point is required. The ‘zero birefringence’ optical filter designs (Yeh, 1980, 1981, 1985) consist of parallel polarizers flanking an anisotropic crystal, resulting in a bandpass filter with maximum transmission at the isotropic wavelength.

Mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$ can in principle be used as birefringent filters, as they exhibit a tunable isotropic wavelength. The simplest version of the Yeh-type zero birefringent filter is shown in the left box of Fig. 5(a). Here, two nearly parallel polarizers flank an x -cut $\text{EDS}_x\text{Se}_{1-x}$ crystal with the optic axis rotated 45° about the azimuth from the transmission plane of the first polarizer. For maximum transmission at the isotropic point of the crystal, the second polarizer must be rotated by an angle φ , equivalent to the optical rotation experienced by light as it propagates through a crystal of thickness d . Fig. 5(c) shows the transmission spectra for two Yeh-type filters using $\text{EDS}_x\text{Se}_{1-x}$ crystals with isotropic points at 364 nm (*i.e.* pure EDSe) and 324 nm ($\text{EDS}_{0.1}\text{Se}_{0.9}$). Transmission spectra were calculated using the Mueller–Stokes calculus, where the polarization state of light is described by a Stokes vector:

$$\mathbf{S} = \begin{bmatrix} I_{\text{tot}} \\ I_0 - I_{90} \\ I_{45} - I_{-45} \\ I_{\text{LCP}} - I_{\text{RCP}} \end{bmatrix}. \quad (4)$$

Here, I_{tot} is the total intensity of the beam, $I_0 - I_{90}$ is the intensity difference between light linearly polarized in the horizontal and vertical azimuthal planes, $I_{45} - I_{-45}$ is the intensity difference between light linearly polarized in the 45° and -45° azimuthal planes, and $I_{\text{LCP}} - I_{\text{RCP}}$ is the intensity difference between left and right circularly polarized light. The Stokes vector is transformed sequentially by the Mueller matrix operators representing the polarizing elements for a particular filter design,

$$\mathbf{S}_{\text{out}} = \prod_{i=1}^n \mathbf{M}_i \mathbf{S}_{\text{in}}. \quad (5)$$

where $\mathbf{M}_i$ is the Mueller matrix of the i th polarizing element in a series of n elements, and $\mathbf{S}_{\text{out}}$ and $\mathbf{S}_{\text{in}}$ are, respectively, the incoming and outgoing Stokes vectors. The total transmission intensity is then the first element of $\mathbf{S}_{\text{out}}$. Assuming input of unpolarized light into the system, the maximum transmission intensity is 50% of the incident light after the first polarizer. Normalizing these spectra is equivalent to doubling $\mathbf{S}_{\text{out}}(1)$. The Yeh-type filters perform poorly as bandpass filters because $\delta\text{LB}/\delta\lambda$ is low for $\text{EDS}_x\text{Se}_{1-x}$ near the isotropic point and generally remains low throughout the visible spectrum.

To improve the performance of $\text{EDS}_x\text{Se}_{1-x}$ mixed-crystal bandpass filters, one might build an analog of the multistage

Figure 5

Optical filter designs. (a) Schematic diagrams of the Yeh and Lyot optical filters utilizing mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$, where S is the light source, d is the thickness of the first mixed crystal (crystals denoted by blue squares), φ is the rotation of the second polarizer (polarizers denoted by lined squares indicating the polarization plane) and D is the detector. [Schematics inspired by Fig. 1 in the article by Aharon & Abdulhalim (2009)]. (b) The expected isotropic point in $\text{EDS}_x\text{Se}_{1-x}$ as a function of the fraction of sulfate in the crystal. (c) Normalized transmission spectra of two Yeh filters. The purple (green) spectrum was calculated for an $200\text{ }\mu\text{m}$ thick x -cut crystal of EDSe ($\text{EDS}_{0.1}\text{Se}_{0.9}$), yielding maximum transmission at 364 nm (324 nm) when φ was equal to about 8° , the pathlength-normalized OR previously measured for pure EDSe perpendicular to $[001]$ (Martin *et al.*, 2017a). (d) Normalized transmission spectra of two corresponding Lyot filters. The solid red (blue) spectrum was calculated for a series of three x -cut crystals of EDSe ($\text{EDS}_{0.1}\text{Se}_{0.9}$) where $d = 250\text{ }\mu\text{m}$, yielding maximum transmission at 364 nm (324 nm) when φ was equal to 0° . The dotted curves represent the corresponding spectra when φ was equal to 8° , resulting in higher transmission at the isotropic wavelength but also higher transmission outside the zeroth-order transmission.

Lyot filter, again accounting for the optical activity of the crystal system perpendicular to the optic axis. Employing three stages of spectral filters, combined with crystal thicknesses of d , $2d$ and $4d$ and a series of polarizers rotated by φ , 3φ and 7φ , yields the transmission spectra outlined in Fig. 5(d). Note that a rotation of the polarizers commensurate with the accumulated optical rotation through the series of mixed crystals is required for maximum transmission at the isotropic point [indicated by dashed lines in Fig. 5(d)], and this rotation would need to be carefully measured for the given mixed-crystal composition. Parallel polarizers ($\varphi = 0$), as indicated by the solid red and blue traces in Fig. 5(d), would result in a small decrease in the transmission intensity at the isotropic wavelength, but significantly damped secondary transmission intensities through the rest of the spectral region, vastly improving the performance as a bandpass filter.

As of writing, commercial bandpass filters with similar performance metrics for peak transmission and spectral specificity in the range of $300\text{--}364\text{ nm}$ are available from optics retailers for several hundred dollars each. The price generally depends on the center wavelength, spectral width, peak transmission and optical density outside of the desired spectral region. For researchers requiring a range of bandpass filters with variable transmission properties in this spectral range, birefringent filters made from mixed crystals of $\text{EDS}_x\text{Se}_{1-x}$ with polarizing films provide a relatively cheap option with a simple fabrication procedure and fully tunable transmission to fill in spectral gaps in the set of commercially available offerings.

4. Conclusions

Ethylenediammonium selenate can be grown as large crystals with near-perfect cleavage. Anion substitution in EDSe may lead to a family of isostructural crystals and mixed crystals with physical properties that can be tailored. Credible applications could well be realized efficiently. Ethylenediammonium forms isomorphous $P4_12_12$ crystals with SO_4^{2-} , SeO_4^{2-} and BeF_4^{2-} , and $P2_12_12$ isostructural crystals with a variety of other anions (Srinivasan *et al.*, 2013; Nichols *et al.*, 2016; Martin *et al.*, 2017a). Here, the simple admixture of sulfate and selenate was demonstrated to tune the wavelength of the isotropic point (accidental isotropy) as a function of composition. From this understanding follows a simple recipe for fabricating a series of bandpass filters extrapolating from the measured optical properties of mixed crystals. Tunable isotropic points could become a target for *ab initio* (Baroni *et al.*, 2001) prediction of the dispersion of crystal refractivities.

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