

Posters - Modulated Structures

P1

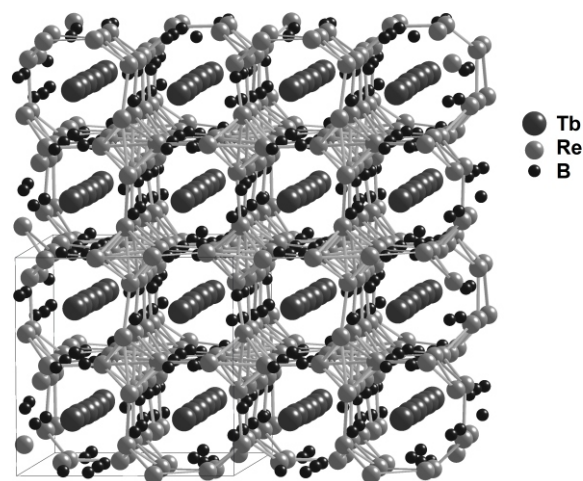
MODULATED COMPOSITE STRUCTURE OF $Tb_{(1+x)}Re_4B_4$ ($x \sim 0.2$)L. Akselrud^{1,2}, Yu. Prots¹, N. Abramchuk¹, Yu. Grin¹¹Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany²Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

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The compound $Tb_{1+x}Re_4B_4$ was prepared by direct reaction of the elements. Pieces of terbium and crystalline boron were placed in rhenium container (in approximate ratio $Ti:Re:B = 1:3.4:3.4$) in argon-filled glove box and arc-melted.

Single crystal diffraction data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD detector applying MoK radiation ($\lambda = 0.71073 \text{ \AA}$). The structure refinement was performed using the WinCsd program package [2]. Main reflections were indexed on the basis of the tetragonal lattice with $a = 10.500(1) \text{ \AA}$, $c = 4.238(1) \text{ \AA}$. All observed reflections were indexed with four integer indices ($hklm$) with respect to the lattice of the $[Re_4B_4]$ substructure applying modulation vector $q = [0 \ 0 \ 1.209]$. The lattice parameters of the composite modulated structure were finally refined on the powder diffraction data: $a = 10.5033(4) \text{ \AA}$, $c_1 = 4.2356(2) \text{ \AA}$, $c_2 = 3.5038(3) \text{ \AA}$, $q = [0 \ 0 \ 1.20885]$.

The total symmetry was described by the tetragonal superspace group $I4_1/amd(00)00ss$. The atomic coordinates in the host sub-structure Re_4B_4 in the space group $I4_1/amd$ were found previously [1] and were confirmed by separate elucidation of this sub-structure with direct methods. The so-obtained coordinate values were used as starting for least-squares refinement. For the guest sub-lattice, the non-standard symmetry group $F4/mmm$, with the Tb atoms at the origin. For the addition of the two groups ($I4_1/amd + F4/mmm$) into the superspace group



$I4_1/amd(00ss)$ a shift of the origin for the host structure by $1/4 \ 0 \ 1/4$ was applied. Finally, the crystal structure of $Tb_{1+x}Re_4B_4$ (Figure) was successfully refined as a modulated composite one. This is the first structure of this family refined and verified with the true satellite reflections.

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P2

MODULATED CRYSTAL STRUCTURE OF $\text{Eu}_2\text{Rh}_{1-x}\text{Ga}_5$ ($x \sim 0.21$)

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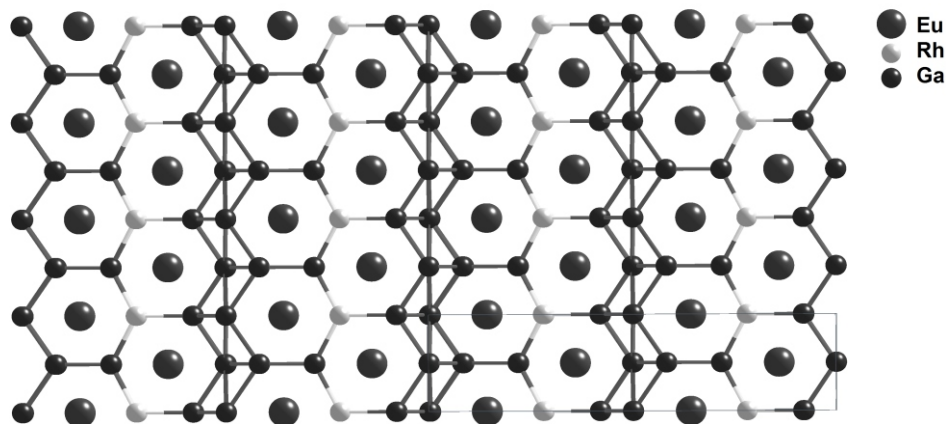
The title compound was prepared by an induction melting of a mixture of elemental components in a glassy carbon crucible under argon atmosphere followed by the thermal treatment in enclosed tantalum tube. The crystal structure was determined by using single-crystal diffraction technique (Rigaku AFC 7 diffractometer, Mercury CCD detector, MoK α radiation, WinCsd program package [1]). The superspace group $Ama2(00)0ss$ with wave vector component of $\tau = 1/2$ and $a = 4.38065(6)$ Å, $b = 18.5019(3)$ Å, $c = 4.29379(8)$ Å, $V = 348.01(2)$ Å³, $Z = 2$ was used for the structure determination and refinement ($R_F = 0.044$ for 1749 unique reflections $hklm$).

The refinement of the structure was performed for two models with a rational wave vector of $\tau = 1/2$ (commensurate modulated) and refined wave vector of $\tau = 0.5009$ (incommensurate modulated).

Description of the structure as a modulated one gets rid of the split positions of the atoms Rh, which are present in

the 3D commensurate superstructure. The crystal structure of $\text{Eu}_2\text{Rh}_{1-x}\text{Ga}_5$ ($x \sim 0.21$, Figure) is a non-centrosymmetric derivative of CeNiSi₂ type [2] with defect positions of transition metal atoms.

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INCOMMENSURATE MODULATION AND THERMAL EXPANSION OF $\text{Sr}_3\text{B}_{2+x}\text{Si}_{1-x}\text{O}_{8-x/2}$ SOLID SOLUTIONS

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Strontium borates and borosilicates attract a great interest as luminescent materials for technical applications. In $\text{SrO}-\text{B}_2\text{O}_3-\text{SiO}_2$ system, properties of glasses and crystalline compounds have been studied extensively [1, 2]. Incommensurate modulated crystal structures of $\text{Sr}_3\text{B}_{2+x}\text{Si}_{1-x}\text{O}_{8-x/2}$ solid solutions ($x = 0.28, 0.53, 0.78$) in

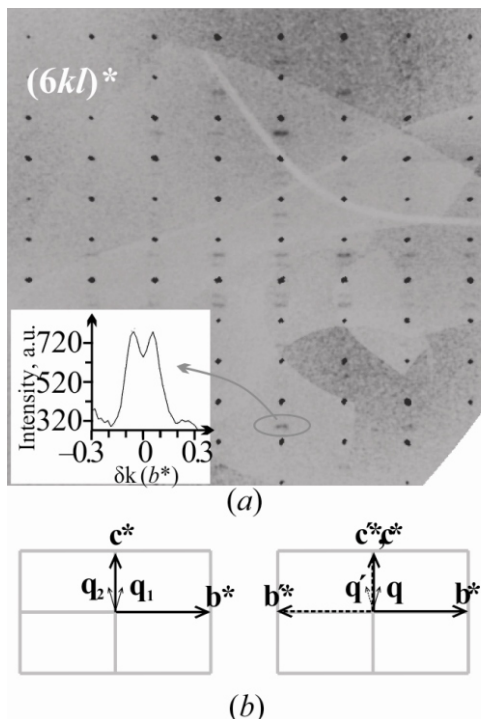


Figure 1. The $h = 6$ plane of the reciprocal space for $\text{Sr}_3\text{B}_{2+x}\text{Si}_{1-x}\text{O}_{8-x/2}$, $x = 0.78$ (a). Partially overlapped profiles of 60–410 and 60–401 satellites are presented in the left lower corner. Modulated crystal can be described in the superspace either as a (3+2)D orthorhombic single crystal (b, left) or a (3+1)D monoclinic twin (b, right) which reciprocal lattices are turned around the c^* axis through 180° .

the $\text{Sr}_3\text{B}_2\text{SiO}_8-\text{Sr}_2\text{B}_2\text{O}_5$ section of the $\text{SrO}-\text{B}_2\text{O}_3-\text{SiO}_2$ system are refined using single-crystal X-ray diffraction data (Fig. 1). Basic orthorhombic structures of the solid solutions are similar to that of $\text{Sr}_3\text{B}_2\text{SiO}_8$ (Krzhizhanovskaya *et al.*, 2010). Crystals of the $\text{Sr}_3\text{B}_{2+x}\text{Si}_{1-x}\text{O}_{8-x/2}$ solid solutions ($x = 0.53, 0.78$) were refined in the $Pnma(0\ 0)00(0\ 0)000$ superspace group with JANA2006 program [3] starting from the positional parameters of $\text{Sr}_3\text{B}_2\text{SiO}_8$ [4]. Unfortunately, the mixed satellites ($h, k, l, \pm 1, \pm 1$) cannot be observed because of their low intensities. Since no strong

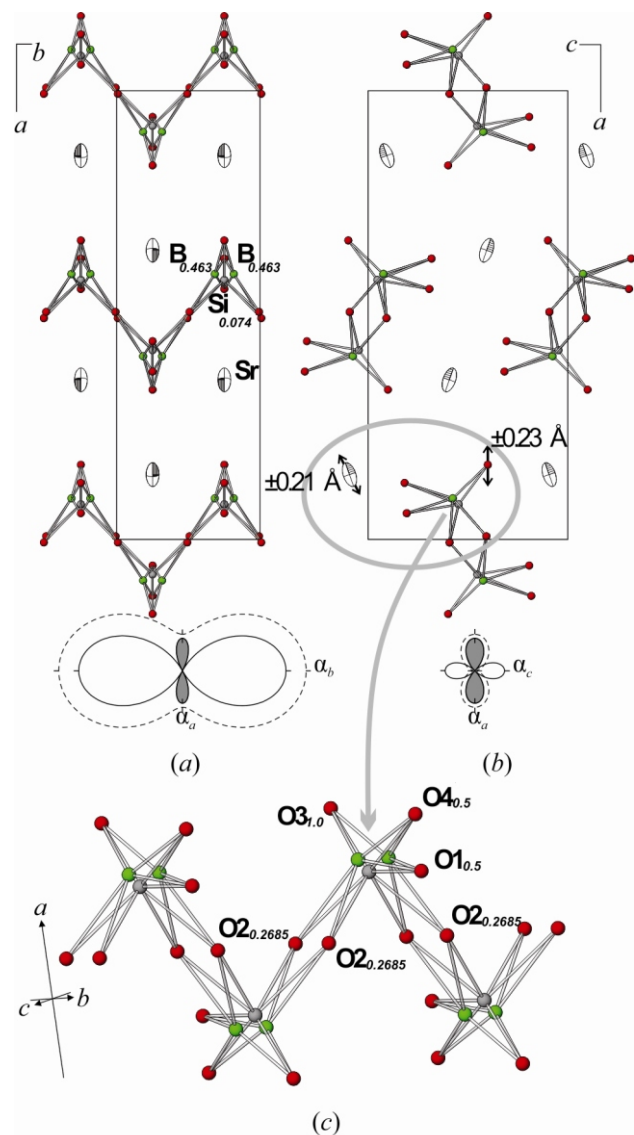


Figure 2. Projections of the average crystal structure of $\text{Sr}_3\text{B}_{2.78}\text{Si}_{0.22}\text{O}_{7.61}$ onto the ab (a), ac (b) planes in comparison to the pole figure of thermal expansion coefficients and a part of borosilicate pseudo-chain (c). The pole figures for 400 and 1300 K are shown in solid and dashed lines, respectively. Displacements of Sr and O1 atoms from their average positions are shown in encircled fragment of the ac -projection. Italic numbers near the atom labels are the site occupancies. Ellipsoids of Sr atoms are drawn at 94 % probability level.



evidence was produced for two-dimensional modulation, another model should be examined. The crystals can be described as twin formed by monoclinic components, each of them corresponds to the (3+1)D symmetry group $P2_1/n(0)$. Twin domains are turned to each other through 180° either around the b or around the c axis. However structure refinement in the monoclinic group does not improve significantly the reliability factors. Thus the preference is given to the (3+2)D symmetry group.

Crystal structure is composed by corner-sharing disordered BO_3 triangles and SiO_4 tetrahedra. Structure modulation is mainly associated with (B,Si)-polyhedra in various orientations (Fig. 2). Presumably, the B_2O_5 groups, same as in $\text{Sr}_2\text{B}_2\text{O}_5$ structure contribute to the solid solution construction. Different orientations of these groups can lead to the structural strains and modulations.

Thermal expansion of $\text{Sr}_3\text{B}_{2+x}\text{Si}_{1-x}\text{O}_{8-x/2}$ solid solutions is strongly anisotropic: $\alpha_a = -8$, $\alpha_b = 21$, $\alpha_c = 8 \times 10^{-6} \text{ K}^{-1}$ at 303 K for $x = 0.78$. Anisotropy decreases on heating: $\alpha_a =$

7 , $\alpha_b = 33$, $\alpha_c = 2 \times 10^{-6} \text{ K}^{-1}$ at 1300 K for $x = 0.78$. The anisotropy also decreases with decreasing of the boron content: $\alpha_a = -4$, $\alpha_b = 19$, $\alpha_c = 10 \times 10^{-6} \text{ K}^{-1}$ at 303 K for $x = 0.28$. The reason for the strong anisotropy of thermal expansion is the preferable orientation of the BO_3 triangles. The expansion is minimal or close to zero within the triangle plane.

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P4

NEW INCOMMENSURATE MODULATED STRUCTURES IN THE SCHEELITE FAMILY

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Scheelite (CaWO_4) related compounds $(A'A'')_n [(B',B'')\text{O}_4]_m$ with $B', B'' = \text{W}$ and/or Mo are promising new materials for red phosphors in pc-WLEDs (phosphor-converted white-light-emitting-diode) and solid-state lasers. Recently a new application field has emerged for these materials due to their ability to visualize temperature gradients with high accuracy and spatial resolution, making them excellent thermographic phosphors [1]. Scheelites can be prepared with a large concentration of vacancies in the A sublattice, giving compositions characterized by a $(A'+A''):(B'\text{O}_4+B''\text{O}_4)$ ratio different from 1:1. The creation of cation vacancies in the scheelite-type

framework and the ordering of A cations and vacancies are a new factor in controlling the scheelite-type structure and properties. Very often the substitution of Ca^{2+} by M^+ and R^{3+} ($R^{3+} =$ rare earth elements) in the scheelite-type structure leads to switching the structure from 3D to (3+ n)D ($n = 1, 2$) regime.

The creation and ordering of A -cation vacancies and the effect of cation substitutions in the scheelite-type framework are investigated as a factor controlling the scheelite-type structure and luminescent properties. For example, the MoO_4 -based $\text{CaGd}_{2(1-y)}\text{Eu}_{2y}(\text{MoO}_4)_{4(1-y)}$

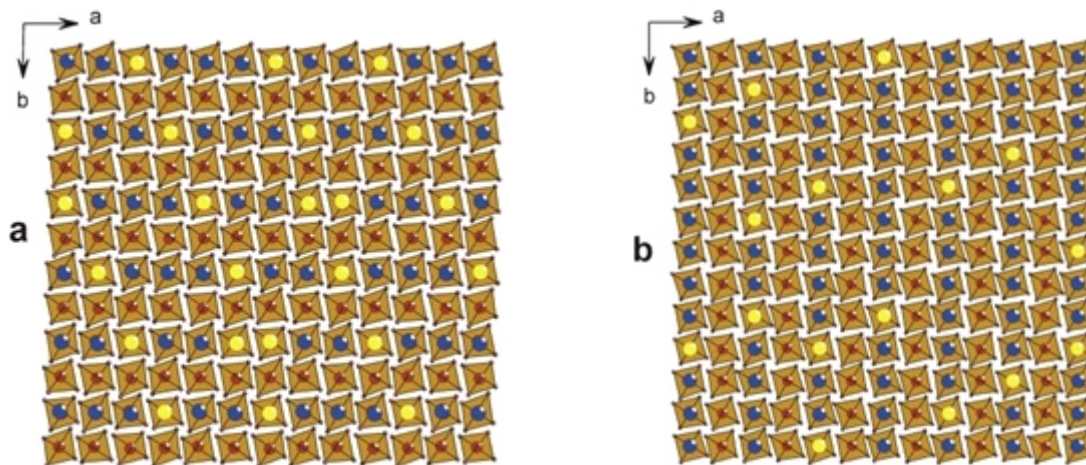


Figure 1. Overview of the crystal structures of $\text{CaEu}_2(\text{WO}_4)_4$ (a) and $\text{CaEu}_2(\text{MoO}_4)_4$ (b).

$(\text{WO}_4)_{4y}$ ($0 \leq x \leq 1, 0 \leq y \leq 1$) solid solutions have (3+2)D incommensurately modulated structures with superspace group $I4_1/a(-, 0)00(-, 0)00$, while the structures of all tungstates are (3+1)D incommensurately modulated with superspace group $I2/b(0)00$. The replacement of the smaller Gd^{3+} by the larger Eu^{3+} at the A -sublattice does not affect the nature of the incommensurate modulation, but an increasing replacement of Mo^{6+} by W^{6+} switches the modulation from (3+2)D to (3+1)D regime [2].

The incommensurately modulated crystal structures of the scheelite-based $\text{CaEu}_2(\text{BO}_4)_4$ ($B = \text{Mo}, \text{W}$) red phosphors have been refined from high resolution synchrotron powder X-ray diffraction data [3]. In both cases the modulation arises from ordering of the Ca/Eu cations and the cation vacancies at the A -sublattice of the parent scheelite ABO_4 structure. The cation ordering is not complete and better described with harmonic rather than with step-like

occupational modulation functions. The structures respond to the variation of the effective charge and cation size at the A position through the flexible geometry of the MoO_4^{2-} and WO_4^{2-} tetrahedra demonstrating an alternation of stretching the B -O bond lengths and bending the O- B -O bond angles.

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P5

STATISTICAL DESCRIPTION OF DIFFRACTION PATTERN OF HARMONICALLY MODULATED STRUCTURES

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Modulated structures are characterized by distortion of atomic positions from the original (periodic) structure. As a consequence, a set of satellite reflexions appear in the diffraction pattern along with the main ones [1]. The indexing of such pattern is possible if the additional vector in reciprocal space (called modulation vector) is used. If the modulation vector is given by the irrational number (*e.g.*

1.618) we deal with incommensurately modulated structure. Harmonic modulation takes place if the modulation function is given by a trigonometric function (*e.g.* sine function). In fact, any kind of modulation can be approximated by Fourier expansion [2]. For incommensurate modulation vectors the diffraction pattern is aperiodic. In case of single modulation component, every atomic positions can be expressed as

$$x_n = na + A \sin(q_0 na) \quad (1)$$

where x_n - atomic position with respect to n -th unit cell; a - unit cell size (parameter of the underlying periodic lattice); A - modulation amplitude; q_0 - modulation vector.

The most successful way of a proper characterization of the diffraction pattern and the structure analysis of MS is the multidimensional (superspace-, n D-) description [3]. This theory is now also widely used for other types of aperiodic systems, like composites or quasicrystals. In the presentation we use the statistical approach. It can be used for structural investigation on both periodic and aperiodic systems, as an alternative to higher-dimensional description. Its equivalence to the latter was analytically proved [4,5] and successfully applied to derive the structure factor

formulae for decagonal [5-7] and, more recently, icosahedral [8] quasicrystals based on model tilings. This approach applies also to aperiodic structures with singular continuous component in the diffraction pattern, *e.g.* based on the Thue-Morse sequence [9] and overlapping clusters [10].

We show that the structure factor formula for 1D harmonically modulated structures derived within statistical approach is given by ordinary Bessel functions of the first kind with kA being the argument of the functions, where A is the modulation amplitude and k - the scattering vector. Scattering vector can be expressed by formula

$$k = nk_0 + mq_0 \quad (2)$$

where integers n and m denote main and satellite peaks, respectively. Vector k_0 is characteristic for the underlying periodic structure ($k_0 = 2\pi/a$).

The envelopes of main peaks are described by Bessel function of order $m = 0$, whereas for the satellite peaks the envelopes are given by Bessel functions of higher-order (see Fig. 1). For each envelope the positions of diffraction peaks form a series with period k_0 . The complete diffraction pattern can be fully described by using two ‘periodicities’: envelopes given by Bessel functions and defining the peaks’ intensities, and periodic series of peaks defining the positions of peaks within the envelope. Finally, we performed a detailed studies on similarities between quasicrystals and modulated structures. We show that 1D quasicrystal, modelled by the Fibonacci chain, can be understood as a modulated structure with multiple modulation vectors being the higher-order Fourier expansion of

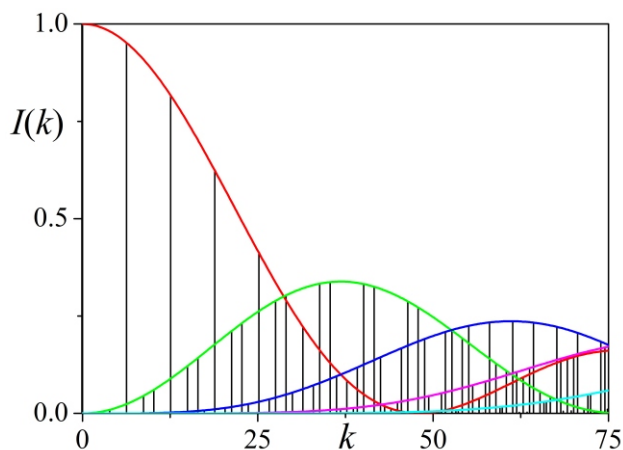


Figure 1. The diffraction pattern with first four envelopes of integer orders m marked. The envelopes are drawn as squared Bessel functions. Envelopes $m = 0, 1, 2, 3, 4$ are marked with red, green, blue, magenta and light blue lines. Parameters in eq. (1) chosen: $A = 0.05$, $a = 1.0$, and $q_0 = 2/a$.

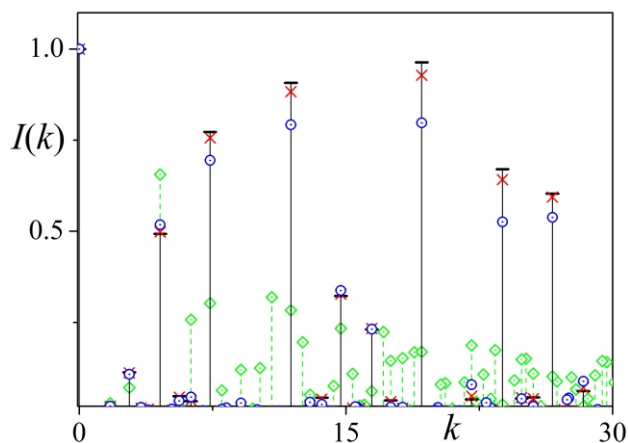


Figure 2. The evolution of the diffraction diagram from 1D harmonically modulated structure with one modulation term (green diamonds), nine modulation terms (blue circles) and fifty modulation terms (red crosses), as defined by eq. (3), to quasicrystal (black bars).

the basic modulation term (see Fig. 2). The full expression for nodes positions of the Fibonacci chain in terms of sine-modulation functions is the following

$$x_n = n(1 - 1/2^2) - \sum_{j=1}^n \frac{1}{j} \sin(jq_0 n(1 - 1/2^2)) \quad (3)$$

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RELATION BETWEEN CHEMISTRY AND MODULATION IN MOLECULAR MATERIALS

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Until recently modulated molecular crystals have largely been ignored by small-molecule crystallographers. Although chemical crystallographers are now becoming increasingly aware of the Devil that lurk in the details of the diffraction pattern, the majority of chemical crystallographers still either close their eyes (i.e. solve the average structure) or throw the crystals away when faced with the indications of an aperiodic structure. With new higher intensity in-house X-ray sources and easier access to synchrotron radiation, more and more molecular structures are showing features beyond the realms of conventional crystallography.

Here we present a study of a phase transition through an incommensurately modulated phase and how the transition

can be affected by changing the chemistry. On cooling, Barluenga's Reagent (bis(pyridine)iodonium(I)tetrafluoroborate) goes through two phase transitions. In the high temperature phase the anion rotates freely, but on cooling the anion partly orders and an incommensurately modulated phase occurs. The low temperature phase is a fully ordered superstructure. Systematically exchanging the anion and halogen showed that modulated phases in these materials are observed with tetrahedral shaped anions though the phase transition temperature varied. Exchanging pyridine with collidine show similar behaviour though the phase transition now happens below 100 K.

P7

TEMPERATURE-PRESSURE PHASE DIAGRAM OF FERROELECTRIC $\text{Sn}_2\text{P}_2\text{S}_6$

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The temperature-pressure phase diagram of the ferroelectric semiconductor $\text{Sn}_2\text{P}_2\text{S}_6$ single crystal has been investigated by neutron and X-ray scattering techniques. The proposed phase diagram was rich in phases, and a special critical point where paraelectric, ferroelectric and incommensurate phases meet was predicted there [1]. We intended to prove the presence of the incommensurate phase by investigating temperature-pressure dependence of satellite and Bragg reflections as well as (quasi)elastic diffuse

scattering. Therefore we have undertaken neutron and X-ray scattering experiments at LLB and ESRF, respectively [2,3]. We found that the $H00$ Brillouin zones are sensitive to the order parameter (polarization) and its fluctuations (see Figure 1). However we have observed only a direct paraelectric-ferroelectric phase transition without any incommensurate phase in the whole investigated pressure range (up to ~ 1.2 GPa) [3]. These results are in a clear disagreement with phase diagrams assumed in numerous earlier works, according to which a hypothetical intermediate incommensurate phase should be present in this region of the temperature-pressure phase diagram.

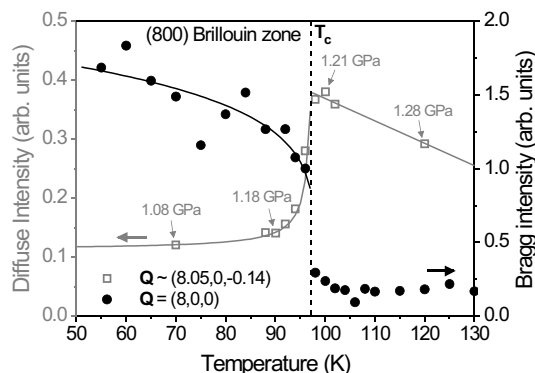


Figure 1. Temperature dependence of critical diffuse scattering and Bragg scattering near a phase transition in the temperature-pressure phase diagram of $\text{Sn}_2\text{P}_2\text{S}_6$ single crystal.

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P8

SOFT CHEMICAL CONTROL OF THE CRYSTAL STRUCTURE AND PROPERTIES OF $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$

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$\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$ [1] is a constituent compound of the wider class $\text{A}_2\text{MO}_2\text{X}_2\text{Ch}_2$ (A = Sr, Ba; M = 1st row transition metal, X = Cu, Ag; Ch = S, Se). Previous work on this compound has included investigation of its potential as a Li^+ ion host in batteries [2] and examination of the solid solution $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_{2-x}\text{Se}_x$ [3]. This work explores topotactic oxidation of the manganese ions to synthesise metastable compositions with larger copper deficiencies [4].

$\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$ was prepared via solid state synthesis, and then copper was deintercalated using varying concentrations of I_2/MeCN solution. The high mobility of copper in this compound meant that a range of copper occupancies could be obtained between 1.5 and 1.33 with a phase gap in the region 1.39 - 1.35.

Reduction in copper content led to changes in the copper vacancy ordering pattern from that described by Adamson *et al.* [3], which only appears at temperatures below an ordering temperature of c. 250 K, to an incommensurately modulated ordering pattern, which is present in room temperature samples. This incommensurate ordering pattern was solved using a $(3+1)\text{D}$ model approach, with modula-

tion vector $\mathbf{q} = 0.2418 \mathbf{a}_0^*$ and space group Xmmm (00)00s. It was found that, as well as occupational modulation of the Cu atoms, there was also significant positional modulation of the oxide layers, which moved closer to the $[\text{Cu}_2\text{S}_2]$ layers to ensure that the S atoms did not become underbonded in low Cu regions (fig. 1).

The presentation will also describe the effect of tuning composition and structure on physical properties.

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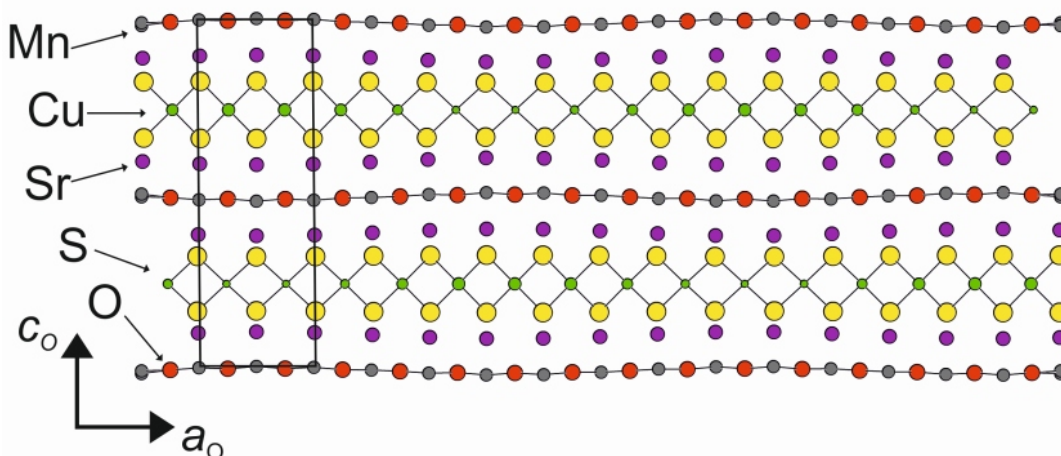


Figure 1. A representation of the modulated structure obtained from analysis of the single crystal diffraction data. The occupational modulation of the Cu sites is depicted using the size of the green circles.

(3 + 1) DIMENSIONAL MODULATED CRYSTAL STRUCTURE OF Cs₃ScSi₆O₁₅**C. Hejny¹, V. Kahlenberg¹ and P. Dabić²**¹University of Innsbruck, Institute of Mineralogy and Petrography, Innrain 52, A-6020 Innsbruck, Austria²University of Belgrade, Laboratory of Crystallography, Djusina 7, 11000 Belgrade, Serbia
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Single crystal X-ray diffraction experiments of Cs₃ScSi₆O₁₅ showed intense Bragg reflections that can be indexed on an *R*-centred hexagonal cell with $a = 13.861(1)$, $c = 6.992(1)$ Å. Inspection of the distribution histograms of the remaining unindexed reflections revealed them to be satellite reflections of up to the third order in \mathbf{c}^* -direction; the satellite reflections are present for $h - k - l + m = 3n$. The modulation wave vector was subsequently defined and refined to $\mathbf{q} = 0.14153(2)\mathbf{c}^*$. This is close to, but distinctly different from $1/7 = 0.142857$. The crystal structure of Cs₃ScSi₆O₁₅ was solved in (3 + 1) dimensional superspace group $X\bar{3}m1(00g)0s0$ from 1838 observed reflections by charge flipping with the program Superflip [1] and refined with the program JANA2006 [2]. Refinement of three modulation waves for positional and ADP values for all atoms converged to *Ro* values for all, main, and satellite reflections of first, second and third order of 0.0200, 0.0166, 0.0181, 0.0214 and 0.0303, respectively

Cs₃ScSi₆O₁₅ has a mixed octahedral-tetrahedral framework structure with six-membered rings of silicon tetrahedra and regular ScO₆ octahedra forming infinite chains along the [0001] direction. According to bond valence calculations ten interatomic distances up to 3.5 Å have to be considered as bondiCng for Cs. All atoms apart from Sc show very large positional modulations with maximum

atomic displacements of up to 0.93 Å. [ScO₆]-octahedra and [SiO₄]-tetrahedra remain rigid with minor variation of interatomic distances. However, as a function of t the [ScO₆]-octahedra and [Si₆O₁₈]-rings rotate around the $\bar{3}$ -axis by over 38° and inter-tetrahedral angles within the Si₆O₁₈ ring diversify greatly. The coordination environment of Cs is very complex with oxygen atoms moving in and out of the Cs coordination in order to maintain the bond valence sum around Cs at a constant level of ca. 1.075.

Cs₃DySi₆O₁₅, $a = 13.996(1)$, $c = 7.1775(6)$ Å, $R\bar{3}m1$ [3] has been described with the same basic structure. However, the statement of positional disorder for Si, O and Cs atoms without further specification leads to the suggestion, that Cs₃DySi₆O₁₅ has a modulated structure similar to Cs₃ScSi₆O₁₅.

The only another Cs-Sc-silicate known to date, Cs₃ScSi₈O₁₉ [4], has a microporous framework structure with an unusual high [TO₄]:[MO₆] ratio of > 6:1.

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P10

STRUCTURE MODULATION IN NLO MATERIALS $\text{Cs}_2\text{TB}_4\text{O}_9$ (T = Ge, Si)

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A new type incommensurate modulated structure of borates was discovered in $\text{Cs}_2\text{TB}_4\text{O}_9$ (T = Ge, Si) using single-crystal X-ray diffraction techniques. The structure were solved by the charge flipping algorithm [1-3] in the superspace group of $I2(0)0$ [4-6]. The result strongly suggests that the structure modulations are mainly associated with the ordering of O5a and O5b atoms, which is controlled by the x_{s4} . And such ordering of O5a and O5b atoms may introduce ordered 3D anionic network of $\text{Cs}_2\text{TB}_4\text{O}_9$ (T = Ge, Si). It is the first time of discovering such kind of modulated borates which appear because of the ordering of borate anions.

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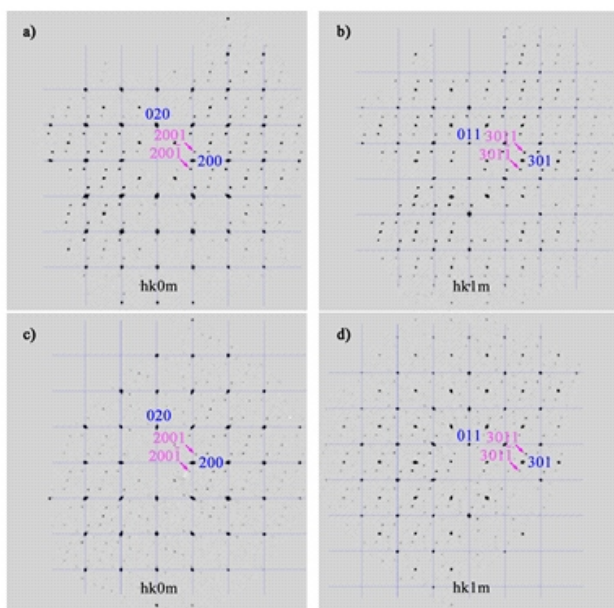


Figure 1. $hk0$ and $hk1$ plan diffraction patterns of $\text{Cs}_2\text{GeB}_4\text{O}_9$ (a-b) and $\text{Cs}_2\text{SiB}_4\text{O}_9$ (c-d). Some main reflections are marked in blue while some satellite reflections are noted by arrow.