The background consists of several overlapping rectangular blocks of color. A large yellow block is at the top. A dark blue block is on the left side, containing the text. An orange block is on the right side, overlapping the yellow and blue blocks. A pink block is at the bottom, overlapping the blue and orange blocks. The bottom right corner is white.

MATERIAL SCIENCES

DEEP UNDERSTANDING AND PREDICTION OF ADVANCED MATERIALS FOR EXTREME RADIATION CONDITIONS

ANATOLI I. POPOV, EUGENE KOTOMIN, ALEKSANDR LUSHCHIK

Fusion reactors attract great interest as a potential source of environmentally clean energy. The radiation-resistant insulators (MgO , Al_2O_3 , MgAl_2O_4 , MgF_2 , BeO , etc.) are of great importance for optical windows, diagnostic measurements, and other fusion reactor applications. From a practical point of view, it is very important to understand and predict their properties and functional characteristics in a very wide range of radiation doses under various radiation particle including a whole range of neutrons, protons, swift heavy and light ions as well as gamma radiation. Material properties are defined by radiation defects therein. Such accurate and objective predictions are especially important, since they are made for conditions that are difficult to verify experimentally and implement, due to both the high costs and the inaccessibility of the corresponding reactors.

This study was performed by the members of theoretical Laboratory of Kinetics in Self-organising Systems at the Institute of Solid State Physics, University of Latvia, and the experimental one at the Institute of Physics (Tartu University, Estonia). These activities were supported by the following projects and research programmes:

a) EUROfusion Enabling Research Programme (ENR-MFE19.ISSP-UL-02 “Advanced experimental and theoretical analysis of defect evolution and structural disordering in optical and dielectric materials for fusion application” (2019–2020), which our group received from EUROfusion as the only one among all the countries of Eastern Europe and the Baltic countries;

b) EUROfusion Functional Materials Programme (WP-15-PPPT-MAT, “Multiscale modelling of radiation effects in MgAl_2O_4 materials and general oxides”, (2014–2020));

c) Latvian Council of Science Grant No. LZP-2018/1-0214 “Radiation damage studies in scintillator materials for high-energy physics and medical applications” (2018–2021)

In a series of papers, the radiation damage evolution and its subsequent thermal annealing was treated as the bimolecular process with equal concentrations of complementary point defects, such as anion vacancies of different charge states and appropriate interstitial defect, which was produced in pairs or cascades by different types of ionizing and particle irradiation – gamma, fast electron, protons, heavy ions or neutron irradiation. Knowledge of the mobility of produced radiation defects, the effect of incident radiation in the conditions of progressive radiation-induced material disordering are absolutely necessary for detailed description of radiation damage. The appropriate migration energies were obtained experimentally or derived from available thermal annealing kinetics for differently irradiated materials. The results obtained are compared with *ab initio* calculations of interstitial anion migration. Two kinds of primary radiation defects – neutral and charged oxygen interstitial atoms in corundum – were discovered and studied for the first time, both experimentally and theoretically.

The kinetics of thermal annealing of the basic electron and hole centres in stoichiometric corundum and spinel irradiated by fast neutrons and protons were analysed in terms of diffusion-controlled bimolecular reactions. Special attention was paid to:

- (1) dose effects on *point defect* annealing;
- (2) a detailed comparison of diffusion-controlled point defect thermal annealing in gamma, neutron, electron and heavy-ion irradiated oxides and halides;

(3) the point defect annealing and metal colloid formation in thermochemically reduced oxides and oxides and halides under irradiation.

Furthermore, properties of single crystals and optical polycrystalline spinel ceramics are compared. It is demonstrated that both transparent ceramics and single crystals, as well as different types of irradiation show qualitatively similar kinetics, but the effective migration energy and pre-exponent are strongly correlated. Such correlation is discussed in terms of the so-called Meyer-Neldel rule known in chemical kinetics of condensed matter. The unusual radiation damage accumulation kinetics under intensive irradiation of oxide materials related to this effect is predicted. This study allows us to prognosticate and control radiation and optical properties of advanced functional materials for fusion applications.

It is important to note that the results obtained turned out to be so interesting and promising for Eurofusion that our two new projects again received funding from EUROfusion Consortium in the framework of the Horizon 2020 research Programmes.

In particular, new projects are guided by a detailed analysis of the influence of structural and radiation defects in dielectric materials. Special attention will be devoted to the analysis of defects in large dielectric mirrors made of diamond with very large dimensions up to 20 cm in diameter. As before, this work is carried out in close collaboration with scientists from Karlsruhe Institute of Technology, Germany under the leadership of Prof. Dr. Theo Scherer. The main results are published in leading journals including *Scientific Reports*, *Journal of Chemical Physics*, *Nuclear Instruments and Methods*, etc. [1–12].

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STUDY OF STRUCTURE-PROPERTY RELATIONSHIP IN THE VERSATILE COPPER MOLYBDATE

INGA PUDŽA, ALEKSEJS KUZMINS

Smart materials have properties that can be affected in a controlled manner by external stimuli. For instance, they can respond to light, temperature, pressure, pH, electric and magnetic fields. Due to their pronounced functional properties, smart materials find applications in various technologies including coatings for glasses and windows, security markers, sensors to control environmental conditions, etc.

Molybdates and tungstates with a general chemical formula ABO_4 ($A = Co, Ni, Cu, Zn, \text{ etc.}$ and $B = Mo, W$) belong to a wide class of functional materials with interesting and potentially useful properties. Among them, copper molybdate ($CuMoO_4$) and its solid solutions are some of the most fascinating multi-

functional materials that exhibit thermochromic (temperature-induced colour change) [1], piezochromic (pressure-induced colour change) [2], halochromic (pH-induced changes in colour) [3], thermosalient [4], catalytic [5] and antibacterial [6] properties (Fig. 1).

The physical properties of $CuMoO_4$ depend on temperature and/or pressure and can be also affected by modifying its chemical composition and morphology. In particular, considerable attention has been paid in the past to colour-related properties of $CuMoO_4$ in the context of sensing applications. Possible chromic applications of $CuMoO_4$ -based materials extend from user-friendly temperature

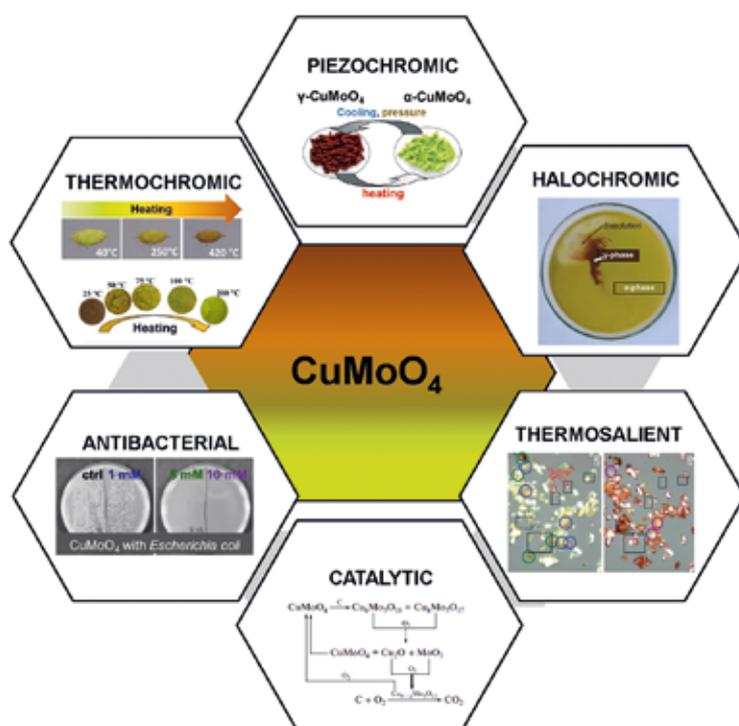


Fig. 1

A schematic representation of $CuMoO_4$ functional properties reported in literature: thermochromic (adapted from [1]), piezochromic (adapted from [2]), halochromic (adapted from [3]), thermosalient (adapted from [4]), catalytic [adapted from [5]] and antibacterial (adapted from [6])

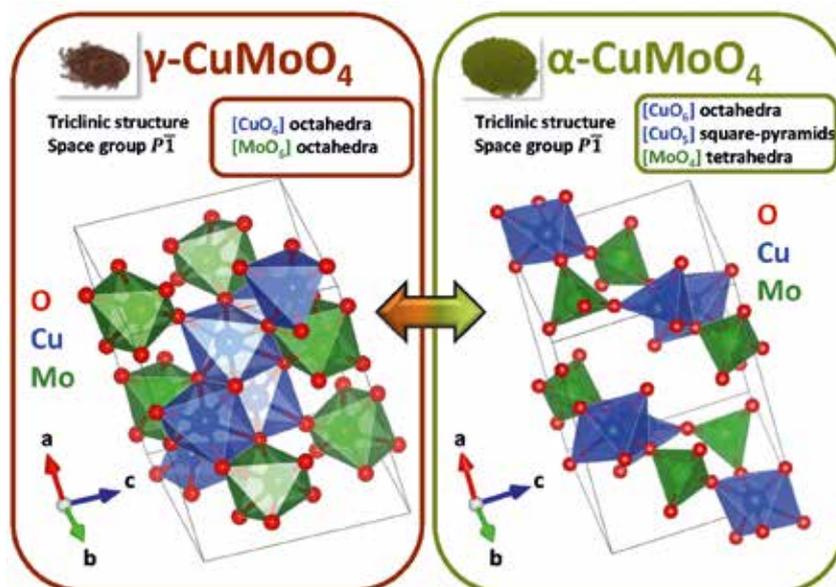


Fig. 2 The unit cell of the low-temperature γ -phase and high-temperature α -phase of CuMoO_4 . The polyhedra forming the structure are indicated. Photographs of corresponding powder samples are also shown

and pressure indicators to cost-effective “smart” inorganic pigments, light filters and sensors [2, 3, 7–9].

Pure CuMoO_4 possesses thermochromic properties both at low (100–300 K) and high (400–700 K) temperature ranges but the origin of the colour change is different. At low temperatures, CuMoO_4 exhibits a reversible structural phase transition between α and γ phases with a hysteretic behaviour, which is accompanied by a drastic colour change between greenish and brownish (Fig. 2). At high temperatures, the molybdate also changes its colour from greenish to brown, but no phase transition is observed.

The thermochromic properties of CuMoO_4 and related materials are closely connected to the local atomic structure of the constituting metal ions. Therefore, the knowledge of their structure is crucial for understanding and optimising their properties, which ultimately determines their practical applications.

X-ray absorption spectroscopy (XAS) is a powerful technique providing valuable information on the local atomic and electronic structure as well as the local lattice dynamics in the material of interest. When combined with a bright synchrotron radiation source, it becomes an ideal tool for studying crystalline and disordered solids, liquids, and gases [10, 11]. In complex materials, XAS allows one to ex-

plore the local environment around particular chemical elements at both high and low concentrations. Furthermore, materials can be studied by XAS at different environmental conditions, i.e. different temperatures, pressures, electric and magnetic fields [10]. Operando and time-dependent XAS experiments are also possible [11]. The structural information in XAS spectra is encoded in tiny fluctuations of the X-ray absorption coefficient, known as the extended X-ray absorption fine structure (EXAFS). The interpretation of the experimental EXAFS spectra is based on the multiple-scattering theory [12] and might be challenging [13], especially for low-symmetry materials as tungstates and molybdates. This analysis often involves high-performance computing due to the huge amount of computations that must be performed.

Further, we summarise the main findings of the systematic study of CuMoO_4 that allowed us to elucidate its structure-chromic property relationship. First, we describe the phase transition below room temperature. Then the possibility to affect the phase transition temperature by chemical doping is discussed. Finally, the evolution of the structure upon heating above room temperature up to 973 K is analysed. Both high (α) and low (γ) temperature phases of CuMoO_4 have a complex triclinic structure. α -phase

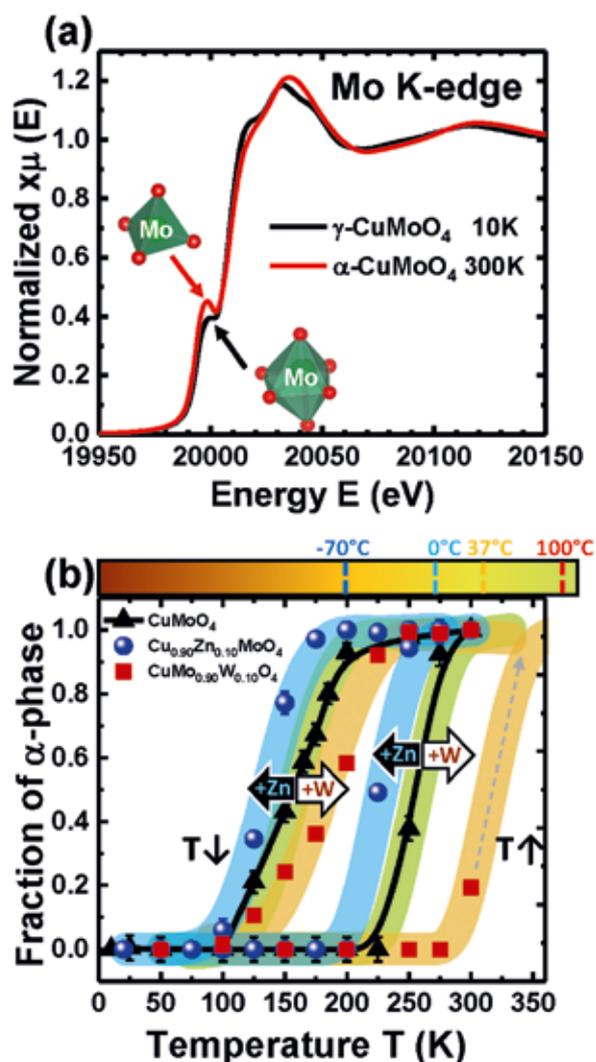


Fig. 3

(a) The Mo K-edge X-ray absorption spectra of α - CuMoO_4 and γ - CuMoO_4 with tetrahedral and octahedral coordination of molybdenum atoms, respectively. (b) The fraction of α -phase as a function of temperature for CuMoO_4 , $\text{Cu}_{0.90}\text{Zn}_{0.10}\text{MoO}_4$ and $\text{Cu}_{0.90}\text{W}_{0.10}\text{O}_4$. The hysteresis loops of the α -to- γ phase transition are highlighted. The hysteresis shift to higher or lower temperatures for solid solutions is indicated with arrows. The gradual colour change between greenish and brownish is illustrated on the top of the graph

is built up of distorted CuO_6 octahedra, CuO_5 square-pyramids and MoO_4 tetrahedra, while γ -phase consists of distorted CuO_6 octahedra and MoO_6 octahedra. The unit cells of both structural phases are illustrated in Figure 2.

Temperature-dependent XAS study of pure CuMoO_4 in the low-temperature range (10–300 K) [14, 15] revealed changes in the local structure around metal atoms during the structural phase transition between α and γ phases. The Mo K-edge X-ray absorp-

tion spectra are strongly sensitive to the coordination of molybdenum atoms (Fig. 3 (a)). The analysis of the experimental data allowed us to reconstruct the hysteresis of the α -to- γ phase transition in CuMoO_4 (Fig. 3 (b)). Molybdenum atoms change their coordination from tetrahedral (in α -phase) to octahedral (in γ -phase) at ~ 143 K upon cooling and back to the tetrahedral environment when heated above ~ 255 K. We found that, in the low-temperature range, static changes of the local environment around Mo atoms are responsible for chromic properties, while the influence of thermal effects is weak.

While the α -to- γ phase transition in CuMoO_4 is well pronounced, the temperature range of its hysteresis is potentially interesting only for the limited number of practical applications. Fortunately, the properties of pure copper molybdate can be adjusted, for instance, by chemical doping [7]. Close ionic radii of Mo^{6+} and W^{6+} ions [16] facilitate the formation of $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ solid solutions. It is also possible to substitute Cu^{2+} ions with other divalent ions, for instance, Zn^{2+} , Co^{2+} and Mg^{2+} .

Composition-dependent XAS experiments were performed to study the influence of W^{6+} and Zn^{2+} ions on the thermochromic properties of polycrystalline $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ and $\text{Cu}_{1-x}\text{Zn}_x\text{MoO}_4$ solid solutions in [17, 18]. We observed that the addition of 10 mol% of tungsten to CuMoO_4 promotes local distortions and stabilises the low-temperature γ -phase, leading to an increase of the phase transition temperature by ~ 50 -100 K (Fig. 3 (b)). As a result, the α -to- γ phase transition takes place at ~ 190 K while γ -to- α phase transition occurs at ~ 340 K. It should be noted that it is also possible to stabilise the γ -phase of $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ with a low tungsten content ($x < 0.15$) at ambient conditions by cryogenic quenching (for example, treatment with liquid nitrogen) [1]. The possibility to obtain a material that changes its colour, for instance, close to the water boiling point may find applications in daily life.

The role of tungsten ions on the structure and thermochromic properties of CuMoO_4 was studied in detail by multi-edge (W L_{3} -edge and Cu/Mo K-edges) X-ray absorption spectroscopy [15] and resonant X-ray emission spectroscopy (RXES) [19]. It was demonstrated that the analysis of the RXES plane provides valuable information on the coordination of

tungsten atoms in the material due to the high energy resolution of the method. It was found that tungsten ions in $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ solid solutions have always octahedral coordination in samples with $x > 0.15$. At the same time, for $x < 0.15$, tungsten ions co-exist in the octahedral and tetrahedral environment at room temperature but their coordination changes to octahedral upon cooling. Preference of tungsten ions to form the octahedral environment, as compared to molybdenum ions, was evident. A change in the tungsten coordination from tetrahedral to octahedral affects the optical properties of the material. The band gap is smaller (and material is darker) in the case of octahedral coordination of tungsten, i.e. at higher tungsten content or lower temperature.

The substitution of Cu^{2+} ions by Zn^{2+} ions [18], in turn, stabilises the α -phase, which is natural for α - ZnMoO_4 . The substitution modifies the electronic structure of the $\text{Cu}_{1-x}\text{Zn}_x\text{MoO}_4$ solid solutions due to the first-order Jahn-Teller effect for $\text{Cu}^{2+}(3d^9)$ ions and its absence for $\text{Zn}^{2+}(3d^{10})$ ions. In $\text{Cu}_{0.90}\text{Zn}_{0.10}\text{MoO}_4$, the α -to- γ phase transition takes place at ~ 134 K and γ -to- α phase transition at ~ 226 K. Note that only α -phase exists at room temperature, thus once the material reaches room temperature it becomes greenish, and it must be cooled down significantly (below ~ 200 K) to change its phase and colour. Such a material with an irreversible colour change in a certain temperature range could serve as a time-temperature indicator, warning if at some point in time the temperature has exceeded the limit.

In the low-temperature range, the considerable optical contrast between the two polymorphic phases and the possibility to tune the thermochromic properties of CuMoO_4 to a more desired and accessible temperature ranges by doping may be the key for the material to serve as a robust indicator for monitoring storage or processing conditions of temperature-sensitive products (food, drugs, vaccines, chemicals, biological materials, etc.). At the same time, such inorganic materials with a thermochromism at high temperatures (above 400 K) attract much attention because of their potential applications for temperature sensing in the ranges where the majority of commonly used thermochromic organic compounds and liquid crystals are unstable.

In the high-temperature range (above room temperature), in contrast to low temperatures, the heating has a stronger effect on the local environment of copper atoms than molybdenum atoms, while the colour also changes from greenish to brownish. The evolution of α - CuMoO_4 structure upon heating was investigated by analysing the Cu and Mo K-edges X-ray absorption spectra using the reverse Monte-Carlo method with an evolutionary algorithm approach (RMC/EA) [20]. This approach made it possible to obtain three-dimensional models of the structure, including the effects of the thermal disorder. We found [21] that the local environment of copper atoms is more susceptible to thermal disorder than the environment of molybdenum atoms. The heating decreases the correlation in the motion between copper and nearest axial oxygen atoms in CuO_6 octahedra, whereas MoO_4 tetrahedra behave as rigid structural units. This dynamic effect is, apparently, the main reason for the temperature-induced changes in the $\text{O}^{2-} \rightarrow \text{Cu}^{2+}$ charge transfer processes and, thus, underlies the thermochromic properties of α - CuMoO_4 when heated above room temperature.

To summarise, the impact of the local atomic structure and lattice dynamics on the thermochromic properties of copper molybdate and its solid solutions was studied using synchrotron-based X-ray absorption spectroscopy. The thermochromic effect below room temperature is caused by the α -to- γ structural phase transition whereas above room temperature the α -phase remains unchanged but thermal disorder plays an important role. The control of the α -to- γ phase transition temperature was achieved by chemical doping and the formation of $\text{CuMo}_{1-x}\text{W}_x\text{O}_4$ and $\text{Cu}_{1-x}\text{Zn}_x\text{MoO}_4$ solid solutions. Hysteretic type of the transition together with its tunability could be useful for an application of the material as a cheap and robust indicator for monitoring storage or processing conditions of temperature-sensitive products, however, in the future, more knowledge about the cyclability and the possibilities of achieving higher temperature resolution will be required. CuMoO_4 has surprised the scientific community with its versatile properties, and we believe that one day it will find its place in some smart systems for daily applications.

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COBALT-CATALYSED C-H BOND FUNCTIONALISATION OF AMINO ACID AND AMINO ALCOHOL DERIVATIVES

LIENE GRIGORJEVA, JEKATERINA BOŠAKOVA, LŪKASS TOMASS LUKAŠĒVICS, ALEKSANDRS ČIŽIKOVS

Chemistry is a science of molecules and transformations between them. Some reactions proceed in a blink of an eye, whereas sometimes a reaction rate may vary from one week to ten years. To increase the reaction rate, scientists have developed different rate-increasing chemical compounds – catalysts. The main advantage of using catalysts is that they are not consumed during the reaction and remain unchanged after its completion. This property allows one catalyst molecule to deliver one molecule of the desired product from one molecule of the starting material and then take the second molecule, the third one, and so on, continuing the catalytic cycle until all of the starting material molecules are consumed. As a result, a very small amount of catalyst is required for the reaction to proceed fast and productively.

The term 'Carbon-Hydrogen (C-H) bond functionalisation' is often used in the field of organic chemistry to describe a chemical transformation where the carbon-hydrogen bond presented in the molecule is broken to be replaced with another one: carbon-carbon (C-C), carbon-nitrogen (C-N) bonds etc. [1]. In contrast to the classical organic chemistry methodology, C-H bond functionalisation approach allows one to skip long-reaction sequences and obtain the desired product in a considerably faster and cheaper manner (Fig. 1). This approach to synthesise molecules is a relatively new addition to the field of the organic synthe-

sis and nowadays is used both in academia and industry to construct highly valuable products.

Unfortunately, these kinds of transformations may not always be performed due to low reactivity of C-H bonds. To overcome this problem, chemists have invented a new approach towards C-H bond functionalisation reactions, employing metal catalysts. Ruthenium (Ru), rhodium (Rh), or palladium (Pd) are proven to be very efficient at accelerating these types of reactions, making them to be the most used catalysts in the industry. On the other hand, these noble metals sometimes may be toxic and their abundance in Earth's crust is very limited, which makes them very expensive [2]. As a solution to this, the development of methods employing less toxic and more earth-abundant metal catalysts such as nickel (Ni), copper (Cu), or cobalt (Co) is of great desire.

Cobalt is an earth-abundant and non-toxic element with the symbol Co and atomic number 27. It plays an essential role in mammal biological processes in the form of cobalamin (vitamin B12) [3]. Historically, the first organic chemist who used cobalt as a catalyst in the C-H bond functionalisation reaction was Murahashi in 1955 [4]. Since then, over 60 years of study turned this transition metal into one of the most promising catalyst for C-H bond functionalisation reactions.

Our research is dedicated to the development of new methodologies for the amino acid and amino alcohol C-H bond functionalisation, employing Co as a reaction catalyst. Amino acids are a great subject of our research for multiple reasons. First, a large variety of natural amino acids can be easily isolated from natural products, which makes them a relatively cheap starting material that can be transformed into more valuable products. Second, a considerable portion of drug molecules used in pharmaceutical industry contain one or more amino acid fragments; thus a development of novel methodologies where unnatural amino acids can be easily obtained, may potentially

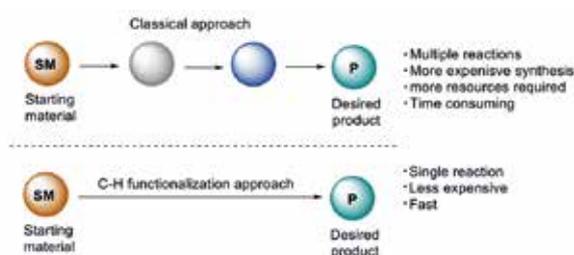


Fig. 1
C-H functionalisation vs classical approach

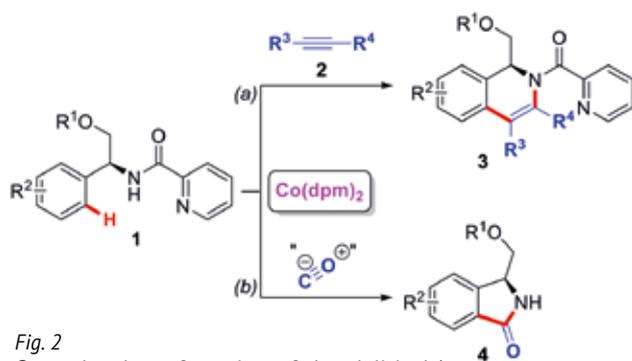


Fig. 2
Co-catalysed transformations of phenylglycine **1**

play an essential role in more rapid development of the medicinal chemistry, synthetic organic chemistry, and biotechnology.

The investigation towards amino acid Co-catalysed C-H functionalisation started with the phenylglycine **1**, derived from glycine – the simplest proteinogenic amino acid (Fig. 2). Initially, reaction with alkynes **2** were performed. Usually, it is a difficult task to achieve the desired transformation with a very good product yield. In our case it was not easy either, thus in a series of more than 700 different reactions the best reaction conditions were finally found. This newly developed catalytic system enabled us to obtain desired products tetrahydroisoquinolines **3** in high yields without the decomposition of the starting materials **1** (Fig. 2a) [5]. Another approach towards functionalisation of phenylglycine **1** was achieved employing carbon monoxide to obtain isoindolines **4** in very efficient fashion (Fig. 2., b) [6]. Both of the newly obtained products **3** and **4** are very valuable building blocks in medicinal chemistry and the common synthetic routes towards these compounds are limited nowadays. Moreover, an umpteen amount of alkaloids, sedative and anxiolytic drugs as well as dopamines contain isoindolinone and isoquinoline fragments and the development of more convenient approaches towards these compounds could facilitate the drug development industry [7].

Along glycine, phenylalanine was also the amino acid of choice for the C-H functionalisation reactions. Phenylalanine is an essential α -amino acid and its derivatives are often used as starting materials for the total synthesis of a variety of useful alkaloids and drugs. Expanding the applicability of Co catalysis, our group was successful in the development of Co-catalysed carbonylation of phenylalanine **5** in the presence of CO gas (Fig. 3) [8].

Encouraged by the diversity of the amino acids that underwent C-H carbonylation under the developed reaction conditions, we decided to apply our methodology for more challenging substrates, i.e. short peptides (two and three amino acids connected in a linear chain). In the case of peptides usually two main difficulties may occur. First, the larger the compound is, the more difficult it is to achieve the high chemoselectivity of the reaction, which means that different undesired by-products may form. Second, amide bonds within peptide can deactivate the reaction catalyst. Nevertheless, we were pleased to find that our newly developed method could also be used for modification of such starting materials and products were obtained in good yields.

Considering the advantages of Co catalysis from the cost point of view, lower toxicity in comparison to noble metals and good reactivity, the further progress in cobalt-catalysed C-H functionalisation of amino acids is expected in the near future. There is still a lot to be developed in this research field, but at this point, contributions by our team have provided some resources for the further studies in the field. Our team of researchers, led by *Dr. chem.* Liene Grigorjeva, joins single-minded and talented chemists: *Dr. chem.* Jekaterina Boļšakova, *M. sc. ing.* Lūkass T. Lukaševics, and *B. chem.* Aleksandrs Čižikovs. In 2020, this group of young

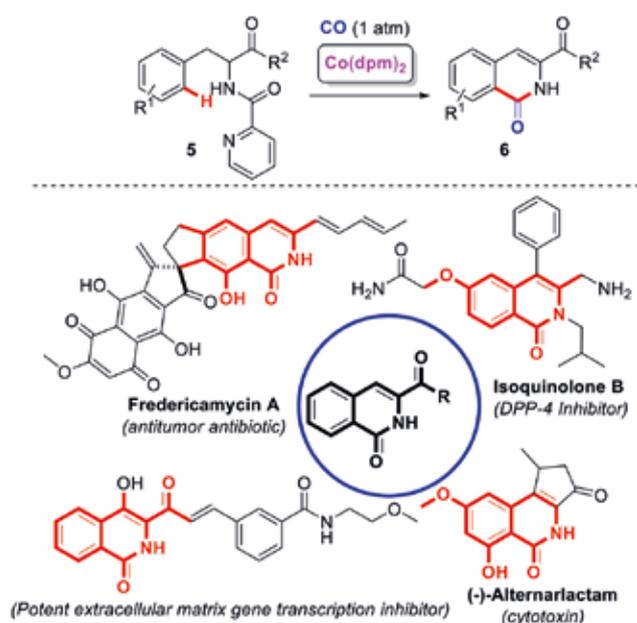


Fig. 3
Co-catalysed synthesis of dihydroisoquinolinones **6** and its abundance in organic compounds

researchers were awarded the Diploma of the President of the Latvian Academy of Sciences for their work on “The Development of Cost-effective and Eco-friendly Methods for the Synthesis of Valuable Organic Compounds”. While working on the project, different conferences were attended to share the group’s results, in addition to being published in the international scientific journals with high impact factors.

In summary, we have developed efficient methodologies for C-H functionalisation of amino acids and amino alcohols based on the inexpensive cobalt catalysis. The demonstrated methods may be used for a broad variety of substrates tolerating different substitution patterns. In addition, short peptides were also applicable thereby offering opportunities for late-stage peptide functionalisation. Besides, the developed methods provide a pathway for accessing valuable organic compounds that can be used in the synthesis of synthetically useful drugs and antibiotic precursors.

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