

CRYSTALLOGRAPHY IN SOUTH-EASTERN EUROPE

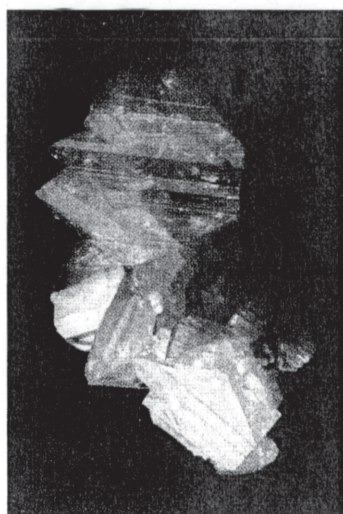
double phosphates of Zr(IV), Hf(IV), Th(IV) and U(IV) with alkali metals.

G. Sijarić, professor of mineralogy and crystallography, was educated at the Inst. of Mineralogy and Petrography of the Natural Faculty of Sciences, Zagreb U. and at the Ruđer Bošković Inst. She obtained a doctoral degree in 1975 from the Faculty of Science and Mathematics of Sarajevo U., under the supervision of S. Šćavničar of Zagreb U. In her thesis, for the first time, she applied quantitative X-ray analyses to bauxites (oxides and hydroxides of Al, Fe, Ti) and silicates (serpentine, zeolites, plagioclases). Their structures and order were defined in plagioclases, and the structures of new minerals and their distribution in Bosnia-Herzegovina was described. In a 1978-1980 project, crystallographic data on numerous minerals, including those from the hundred-years-old collection at the National Museum in Sarajevo, were catalogued. Other targets for study included kidney stones and gall stones of citizens from Sarajevo. G. Sijarić has taught crystallography and mineralogy to chemistry, geology and geography majors at the Sarajevo U., Tuzla and Priština.

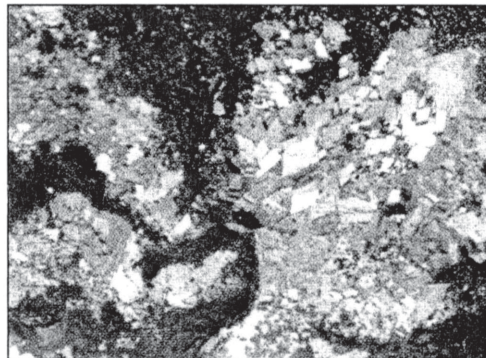
During the war in Bosnia-Herzegovina in the 1990's all instruments and facilities for scientific research were devastated. Because it has not been economically possible to repair or replace the needed instruments, research depends on cooperation with scientists and institutions from neighbouring countries.

At present, there are a few scientists using crystallographic data at the Chair of General and Inorganic Chem., Chem. Depart., Faculty of Natural Sciences. The Head of this group E. Kahrović (emira_kahrovic@yahoo.com) received a PhD for crystallographic characterization and structures of Pb-azides at the Natural Sciences Faculty in Sarajevo in 1996. She now studies synthesis and crystallographic characterization of ruthenium(III) complexes with monobasic (NO) and dibasic (ONO) Schiff bases derived from salicylaldehydes.

Bosnia-Herzegovina currently has no crystallographic Association. Researchers network with the associations in Slovenia and Croatia to gain information about conferences and other events.



Large crystal twins of the mineral hyalophane, $(K,Ba)[Al(Si,Al)Si_2O_6]$ from Busovača, Bosnia and Herzegovina.



Mineral gaspeite, $(Ni,Mg,Fe)CO_3$, from Duboštica, Bosnia and Herzegovina, which was first determined in 1998 (Bermanec, V., Sijarić, G., Kniewald, G., Mandarin, J. A. *Can. Miner.* 38 (2000), 1371-1376).

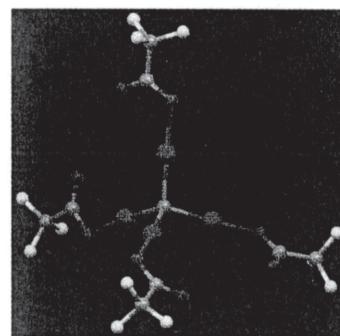
Financial support is very limited. The only X-ray diffraction instruments are in the factories of aluminum in Mostar and alumina in Zvornik, where they are used for quality control.

Crystallography in Macedonia

BY GLIGOR JOVANOVSKI (gligor@pmf.ukim.mk) AND PANCE NAUMOV (npance@wakate.frc.eng.osaka-u.ac.jp)

The Republic of Macedonia is a small country (~25 700 km²) located in the central Balkan peninsula in South-Eastern Europe, with a population of about 2 million. The first X-ray scattering measurements reported by a Macedonian researcher were those of S. Pocev of the Faculty of Technology and Metallurgy (SS. Cyril and Methodius U.) in Skopje, who worked with G. Johansson at the Royal Inst. of Technology in Stockholm, Sweden. Pocev published the paper "An X-ray Investigation of the Coordination and the Hydrolysis of the Uranium(IV) Ion in Aqueous Perchlorate Solutions" in *Acta Chemica Scandinavica* in 1973. Later, he completed his PhD thesis on structures of mercurated oxonium and sulphonium salts at the U. of Zagreb (1978), and the results were published in the *Journal of the Chemical Society*.

From 1972 through 1974, G. Jovanovski from the Inst. of Chemistry (Faculty of Natural Sciences and Mathematics, FNSM) in Skopje was a student in the X-ray Laboratory of D. Grdenić and B. Kamenar at the U. of Zagreb, where he determined the crystal structure of tetrakis(trifluoroacetoxymethyl)mercury methane, the first example of a carbon atom bound to four mercury atoms. Later, Jovanovski determined crystal structures of metal saccharinate complexes for his PhD thesis at the same University. With J. Thomas (Uppsala U.), he studied the deformation electron density of potassium oxalate monohydrate.



The crystal structure of tetrakis(trifluoroacetoxymethyl)mercury methane (*J. Chem. Soc., Chem. Comm.* 546 (1974), 646-647).

Returning to Skopje in the 1980s, Jovanovski introduced a course in crystallography at the SS. Cyril and Methodius U. in Skopje as a part of the Structure of Molecules major, in the Dept. of Chemistry at FNSM. At that time, two powder diffractometers were available in Macedonia—a *Jeol* instrument at FNSM, and a *Philips* instrument operated by the Faculty of Technology and Metallurgy. The instruments were used for routine analyses, characterization, simple experiments and teaching. In the following years, a small group of crystallography researchers was established at the Inst. of Chemistry, including A. Mirčeva, O. Grupče, P. Naumov and P. Makreski. Sporadically, X-ray diffraction was employed for structure determination and characterization by other members of



From left to right: Petre Makreski, Gjorgji Petruševski, Gligor Jovanovski, Panče Naumov and Tomče Runčevski.

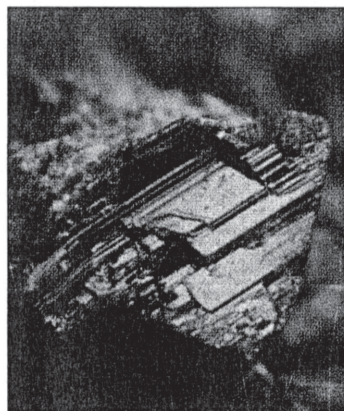
the Inst. of Chem.: B. Šoptrajanov, V. Jordanovska, V. Petruševski, S. Aleksovska, V. Stefov, Gj. Petruševski and T. Runčevski.

When the country was part of SFR Yugoslavia, Jovanovski attended the annual meetings of the Yugoslav Centre of Crystallography, and organized the 1981 meeting in Skopje. Since 1996, Jovanovski has participated in the annual Croatian-Slovenian crystallographic meetings, together with other Macedonian crystallographers (S. Pocev, V. Jordanovska, A. Mirčeva, O. Grupče, P. Naumov and P. Makreski). Recently, a Division of Crystallography was established as part of the Society of Chemists and Technologists of Macedonia.

None of the national or private universities in Macedonia has modern crystallographic equipment. Active Macedonian crystallographers have conducted research in foreign universities, or in collaboration with such institutions. P. Naumov and P. Makreski,

who were mentored by Jovanovski, are currently active in the field. The main studies underway in Macedonia concern chemical crystallography (especially, metal-coordination compounds as models for biological effects of food additives), inorganic compounds (spectra-structural correlations in isomorphous and isotopic series), organic compounds with interesting electronic and optical properties, solid-state reactivity (photochromism and thermochromism), and polymorphism of pharmaceuticals. An *Atlas of Minerals from the Republic of Macedonia*, is to be published soon (in English) by the Macedonian Academy of Sciences and Arts.

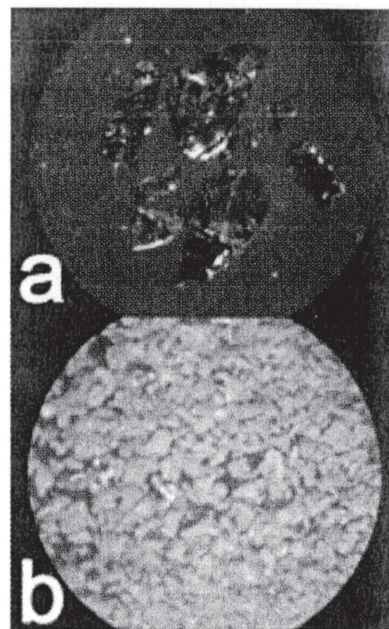
One of the most active research groups of the Division of Crystallography in Skopje (G. Jovanovski, O. Grupče and P. Naumov) has over 40 publications in international journals, which are mainly related to the coordination chemistry of saccharin (an artificial sweetener with suspected carcinogenic activity), thiosaccharin and their mixed complexes with aromatic bases. In 2004 P. Naumov earned a PhD degree in diffraction at the Tokyo Inst. of Technology,



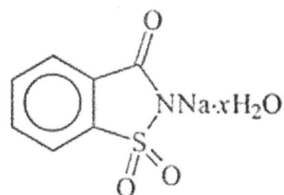
Genuine crystals of the mineral lorandite (TlAsS₂) from Alšar, Macedonia.

under the supervision of Y. Ohashi. He established a laboratory for the study of photoinduced phenomena and solid-state chemistry at the National Inst. for Materials Science in Japan (2004–2007), and now leads a research group at Osaka U. (Japan). In 2009 Naumov was appointed associate professor of the Inst. of Chemistry in Skopje, where he has been spearheading the development of collaborative crystallographic research in Macedonia. The current interests of the group are materials exhibiting photoinduced and thermal phase transitions for (opto)spintronics applications, X-ray photodiffraction and time-resolved diffraction using synchrotron X-rays.

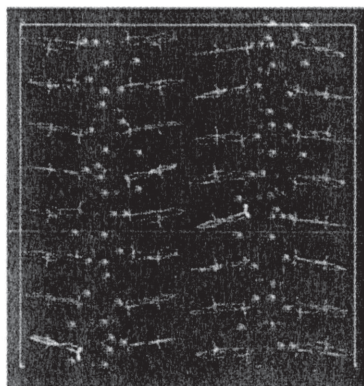
Macedonian crystallographers P. Naumov and G. Jovanovski, together with B. Kaitner (Zagreb), D.A. Rae (Canberra) and S.W. Ng (Kuala Lumpur), determined the crystal structure of the sweetener sodium saccharinate, Na₆₄(C₇H₄NO₃S)₆₄·120H₂O, a commercial compound incorrectly assumed to have been a dihydrate. This extremely complicated modulated structure with a unit cell of 15.6 nm³ and Z' = 16 (Z = 64) was ranked #6 in the World's database of small-molecule structures with high Z' (U. of Durham). The Macedonia research team has also described the first direct observation of an all-solid autocatalytic reaction set, a group of photo-triggered reactions proceeding in the crystals of the natural mineral realgar (*J. Am. Chem. Soc.* **132** (2010), 11398–11401). Ways and means of upgrading crystallographic instruments in Macedonia, are being sought and the advice and assistance of the international community would be greatly appreciated. ❖



Crystals of the genuine Macedonian mineral realgar (As₂S₃) before exposure to visible light (a) and after photochemical conversion to pararealgar (b) (*J. Am. Chem. Soc.* **132** (2010), 11398–11401). Copyright: American Chemical Society.



Sodium saccharinate, NaC₇H₄NO₃S·xH₂O, listed in most catalogues as a dihydrate (x = 2), has been extensively used as a food additive and has constituted the basic component of the diabetics' diet for about 125 years. This crystal structure, with Z' = 16 and a very large unit cell, represents one of the most difficult cases for a small molecular species such as the saccharinate ion. The composition is best described as Na₆₄(C₇H₄NO₃S)₆₄·120H₂O (*Angew. Chem. Int. Ed.* **44** (2005), 1251–1254).



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