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Preface

This chapter of the Journal of Thermal Analysis and Calorimetry is dedicated to the 80th Anniversary of Professor Vladimir Boldyrev, who was born on April, 8th 1927 in Tomsk (Siberia, Russia). The goal of this chapter is to celebrate the life and work of this truly outstanding scientist and educator, to highlight the impact and influence of his scientific contributions on the current thinking and direction of research in the areas of reactivity of solids, thermal decomposition, mechanochemistry. Vladimir Boldyrev is a member of the Russian Academy of Sciences. For 23 years, Vladimir Boldyrev was the director of the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk). He was the first in the USSR to start teaching solid state chemistry as a general course at the university level. Many of his former students became professors and occupy now leading positions in science and industry not only in Russia, but also in Europe, or in the USA. He was a member of the IUPAC Advisory Committee on Inorganic Chemistry (1987-1991), the President of the International Advisory Committee on the Reactivity of Solids (1992–1996), one of the founders and the first President of the International Mechanochemical Association (1988–1997). At the present time, Vladimir Boldyrev is Director of the Research and Education Centre of the Novosibirsk State University, and still has a small research group at the Institute of Solid State Chemistry and Mechanochemistry Russian Academy of Sciences. He gives a lecture course to students of Chemistry Department of the Novosibirsk State University.

Thermal analysis and calorimetry were used as the research tools in many of his studies. He was a member of the USSR National Committee on Thermal Analysis, and represented the USSR in ICTA during several years; he has also been the Chair of the Committee on Solid State Chemistry of ICTA. At the present time, Vladimir Boldyrev is a Board Member of Eurostar-Science – European Society of Applied Physical Chemistry, and until recently he has participated actively in PhandTA Meetings. In 2005 he was awarded a Kurnakov Medal of the Russian Academy of Sciences for his studies of the mechanism and kinetics of solid-state reactions, and the development of the methods of control of the reactivity of solids and the properties of the solid reaction products.

It is a special honor for me to act as an Editor of this Issue – being professor Boldyrev's daughter, I also consider myself as one of his pupils and followers, and was greatly influenced by him as a scientist and a lecturer. I am happy, that several people, who entered the field at the same time as Vladimir Boldyrev did, and who were his friends and colleagues during many years, have accepted my invitation to contribute to this issue. The contribution by professors Andrew Galwey and Michael Brown opens the issue. The two authors are world-recognized as experts in the field of the thermal decomposition and the 'pioneers' of this field. A book by M. Brown, D. Dollimore, A. Galwey 'Reactions in the Solid State' [1] was translated into Russian due to the efforts of Vladimir Boldyrev, who has edited the translation. Professor Luigi Nassimbeni originates from the same scientific school as professor M. Brown does – that of professor E. G. Prout, one of the two famous solid-state researchers, after whom the Prout-Tompkins kinetic equation was named [2, 3]. Professor Vladimir Logvinenko, together with whom professor Boldyrev was involved into the activities of the USSR National Committee on Thermal Analysis, the ICTA and the ESTAC, also continues the tradition of the kinetic description of the reactions of thermal decomposition. They have also cooperated with Vladimir Boldyrev in the studies of the decomposition reactions of coordination compounds [4]. Professor Bernard Delmon focuses his attention on the synthesis of highly dispersed solids and their reactivity, in particular – on the systems related to the heterogeneous catalysis. His approach to the problems is especially close to the style of thinking, which has been typical for professor Boldyrev throughout his life – clear model experiments, to test directly the hypothesis on the detailed mechanism of the reaction, and not just a sophisticated formal kinetic treatment (although professor Delmon is one of the worlds experts in the heterogeneous kinetics, and his monograph on the topic [5] was translated into Russian by the efforts of Professor Boldyrev as the Editor). The joint monograph by professors Boldyrev and Delmon [6] became a classical text-book, which is still very efficiently used for research and education. Professor Shmuel Yariv has served for a long time for ICTA, and it was at the same time, when Vladimir Boldyrev was representing the USSR in the ICTA, and they had many opportunities to meet each other, exchange scientific ideas, and develop also a personal relationship, which has survived after many years. It was professor Shmuel Yariv, who has readily supported the idea of this commemorative issue on behalf of the Journal of Thermal Analysis and Calorimetry, and has contributed to its promotion. Issak Lapides, a co-author of professor Yariv in the contribution to this issue, is also an old friend of professor Boldyrev since the times of the USSR, when he worked in Irkutsk. Professor Mamoru Senna is a very old friend and colleague of professor Boldyrev. They have first met each other in Cracow in 1980, at the 9th International Symposium on the Reactivity of Solids, and then in 1982 in Japan, when professor Boldyrev was visiting professor Wazo Komatsu for two months. It was at that time, that they came to the idea of organizing a series of joint USSR-Japan (later – Russia-Japan) Meetings on Mechanochemistry, the first of which took place in Novosibirsk in 1986. At the present time professor Senna is the President of the International Mechanochemical Association, having followed at this position professor Boldyrev, professor Ivanov (one of professor

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Boldyrev's former students, now at Tosoh, USA), and professor Atzmon. Professor Kostadin Petrov has been the guest of professor Boldyrev in Novosibirsk attending an international meeting 'Contemporary problems of the reactivity of solids' in 1988; they share interest in solid-state synthesis and an enormous sense of humour. The contribution of professor Petrov to this issue deals with combustion. Boldyrev was involved in the research on combustion in the 1960s–1970s in relation to the propellants [7, 8], and came back to the combustion-assisted synthesis of materials in the 1990s–2000s [9–13]. Professor P. Baláž is a younger-co-worker of an old friend and colleague of professor Boldyrev – professor Klara Tkáčova. She was a supervisor of Vladimir Šepelák, who is contributing to this issue as well. The colleagues from Kocise (Slovakia) were collaborating with professor Boldyrev for many years on mechanochemistry of minerals, in particular – of chalcogenes [14]. The present contribution makes an excellent bridge between the past and the very recent research. Professor Laszlo Takacs has co-authored with professor Vladimir Boldyrev several papers on self-propagating mechanochemical reactions [15], and also shares his interest in the history of solid-state research and a taste for clear model experiments.

I am grateful to the representatives of the 'younger generation', who are now developing many of the ideas of Professor Boldyrev, for their readiness to contribute to this honorary issue. Professor Coquerel and his co-authors develop the approach to the solid-state dehydration and desolvation reactions, which is based on a detailed analysis of the crystal structures of the reactants and the products, applying it to pharmaceuticals – the field, to which professor Boldyrev has been contributing in the last decades, after many previous years of successful research of inorganic solids [6, 16, 17]. Vladimir Šepelák, who is now successfully working in Germany, is one of the foreign PhD students of professor Boldyrev. In 1995 he has successfully defended in Novosibirsk his PhD Thesis 'Thermal stability and reactivity of mechanically activated zinc ferrites' under the supervision of professor Vladimir Boldyrev. The contribution to this issue develops the ideas originating from this thesis and the research carried out in Novosibirsk by professor Boldyrev and his co-workers [18–25], and is a nice illustration of what has been achieved in this field during over 10 years of intensive and extensive research. Professor Braga with co-workers and Professor Descamps with coworkers describe examples of successful applications of mechanochemistry to organic systems. This is also one of the topics, which professor Boldyrev himself develops since 1980s [26–40]. The contribution by Dr. V. Drebushchak, Dr. L. Myl'nikova and Professor V. Molodin provides an example of an application of the thermal analysis in archeology and has resulted from a cooperation initiated by professor Boldyrev, in which he has been actively involved himself [41].

The 14 papers cover different topics, but they all represent the variety of the fields in the solid-state research, in which professor Boldyrev has been involved himself for over 60 years already: thermal decomposition, solid-state synthesis, kinetics, mechanisms of solid-state reactions, reactivity of solids, combustion, mechanochemistry of inorganic and organic materials.

As a student of Tomsk State University, Vladimir Boldyrev has started his scientific carrier with the studies of solid-state reactions – the topic, which at that time was absolutely non-popular, in contrast to coal chemistry, or to radical chain reactions. As often happens, this almost accidental choice of a research field has pre-determined the life-long activity. The PhD Thesis of Vladimir Boldyrev (Tomsk State University, 1951) dealt with 'Thermal decomposition of metal oxalates'. In the late 1990s and early 2000s he has summarized his work in the field of the thermal decomposition of oxalates and other inorganic salts in a series of review papers and monographs [42–44]. The work started rather traditionally, with studying the reactions of thermal decomposition of inorganic solids and trying to find the best equations describing the kinetics and giving kinetic parameters. Also nowadays, 60 years afterwards, similar approaches are still in use. For Boldyrev, however, the mechanism of a process was always more interesting than any formal description of this process. Rather soon he became interested in the role of the defects in the solid-state reactions, and this became his field of research for many years [6, 42–58]. His studies of the thermal decomposition became less and less 'formal'; kinetic, thermodynamic, structural aspects of the reactivity were considered in a close interrelation. He started with inorganic solids, but the same approaches were later successfully transferred to coordination compounds, molecular organic solids, including pharmaceuticals [59]. A close cooperation with physicists resulted in many important achievements. Solid-state reactions were shown to be very selectively sensitive to particular types of defects, and this could be used both for the control of the reactivity of solids, and for the studies of the elementary steps of the solid-state reactions. Boldyrev has developed the concepts of the 'localization' and of the 'autolocalization' of the solid-state reactions, which were developed further as the concept of 'feed-back' by his younger co-workers [56–66].

The studies of the thermal decomposition were just the beginning of the research in the field of solid-state reactivity. Solid-state synthesis, intercalation reactions, polymorphic transformations, solubilization of drugs, drug-excipient interactions, synthesis of solids in the metastable forms using the precursor techniques, radiation-assisted thermal synthesis, combustion, microwave chemistry, and, of course, mechanochemistry [26–40, 66–71] – this is a far not complete list of topics covered by the research activities of Vladimir Boldyrev. During the last years, his interests have shifted more and more from inorganic solids to molecular crystals, in particular – to solid drugs. As an expert, he was invited to lecture at Pfizer Inc., and his group was working on a joint project with Pfizer, supported by a grant from the CRDF. He has also done a lot for promoting solid-state chemistry [72].

Although the systems to be studied changed, the main focus remained the same: searching a detailed mechanism of the process and the methods of the control of this process. The results of the fundamental studies, which have now become 'the classics' of the solid-state chemistry, have found important practical applications, ranging from non-silver photographic materials, improved ceramic materials, ionics and intermetallics – to new, ecologically advantages technologies. Boldyrev's group never stopped fundamental research, and, at the same time, it worked successfully for industry in the USSR (and later – Russia), and other countries. Professor Delmon has written in one of his papers published in 1982: 'The discovery of new structures and of materials with new exciting properties continues at a rapid pace. But relatively little is done on reactivity. The words 'chemistry of solids' and 'reactivity of solids tend, nowadays, to describe rather research on structures or physical properties than on kinetics, on the mechanisms by which solids react or on the possibilities one has to control the way they react.' [73]. This sounds even more appropriate today. The life-long experience of Boldyrev's research has proved, that only detailed fundamental studies of the processes eventually result in really innovative applications in the field of materials sciences and technologies.

I hope that you will enjoy reading this issue as much as I have enjoyed putting it together. I can only regret, that my mother did not live long enough, to see this issue. Over 50 years she was with my father, not only as his wife, but also as a co-worker and a colleague in research. My father's success in life and science is to a very large extent due to the assistance and self-sacrifice of my mother. I would like to dedicate this issue also to her memory.

The last but not least – I am grateful to Professor Nikolai Lyakhov, who was one of professor Boldyrev's students and my supervisor, and who is now the Director of the Institute of Solid State Chemistry and Mechanochemistry in Novosibirsk, after he has substituted my father at this position in 1997. It was the idea of Professor Lyakhov to prepare this special issue, and I was happy to take the effort of inviting contributors and assembling the issue.

Elena Boldyreva

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On behalf of the Editors and the members of the Board of the Journal of Thermal Analysis and Calorimetry, we wish Prof. V. Boldyrev good health and long years in science. We also would like to take this opportunity to thank him for his high-level scientific papers he has published and for his efforts as a reviewer. His activities have contributed significantly to the Journal's success.
Many happy returns!

Editors

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