MINERALOGIA POLONICA
Vol. 36, No 1, 2005
PL ISSN 0032-6267

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JANUSZ KRACZKA (1951–2002) AND HIS MÖSSBAUER SPECTROSCOPY CONTRIBUTION TO MINERAL SCIENCE

Janusz Kraczka, born in Kraków on 22nd February, 1951, graduated in Physics from the Jagiellonian University. In 1974 he was employed at the Institute of Nuclear Physics, Department II of Nuclear Spectroscopy, in Kraków. Dealing mainly with Mössbauer spectroscopy, he applied this method in the investigations on the role and properties of iron in various substances, first of all in minerals and rocks. As a result, he developed

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a close cooperation with the Department of Mineralogy, Petrography and Geochemistry, AGH-UST, headed then by Professor W. Żabiński. His other papers concerned processes of iron reduction in iron ores and the reduction of catalysts during ammonia synthesis. J. Kraczka also constructed a range of laboratory equipment utilized in Mössbauer measurements of the iron content, even at its very low concentrations.

In 1984 J. Kraczka obtained his Ph.D. degree, presenting the dissertation "Application of ^{57}Fe Mössbauer spectroscopy in investigations of selected minerals" (supervisor: Prof. Andrzej Hrynkiewicz). He published about 50 papers in renowned journals and conference materials, cooperated with foreign universities (Salzburg, Kiele, Kiev) and numerous Polish industrial institutions.

Untimely death of Janusz Kraczka, a talented but self-effacing person, represented a loss not only for his colleagues from the Institute of Nuclear Physics but also for many mineralogists. Although not being formally a member of the Polish mineralogical community, he made significant contributions to the knowledge of various iron-containing minerals. Some examples of the relevant problems studied by J. Kraczka in cooperation with mineralogists, concerning the position and type of iron ions in silicate minerals, are given below.

TOURMALINES (*A.P.*)

The tourmaline-group minerals are a group of cyclosilicates containing additional B ions and showing a very complex composition, often presented in the form of the general formula:

$$^{[9]}X^{[6]}Y_3{}^{[6]}Z_6{}^{[4]}\,[T_6O_{18}\,(BO_3)_3\,{}^{[4]}V_3\,{}^{[4]}W]$$

where:

$^{[9]}X$ – Na, Ca, □, K, ...; $^{[6]}Y$ – Li, Mg, Fe^{2+}, Mn, Al, Fe^{3+}, Cr, V, Ti, ...;
$^{[6]}Z$ – Al, Mg, Fe^{3+}, Cr, V,...; $^{[4]}T$ – Si, Al, B, ...; $^{[3]}B$ – B, □, $^{[4]}V$ – OH, O,
and $^{[3]}W$ – OH, F, O.

The distribution of iron ions between two various octahedral sites (Y and Z) is the most important structural problem, dealt with Mössbauer spectroscopy (MS). The limited Al–Fe^{3+} disorder at the Y and Z sites has been found in MS studies and corroborated by X-ray structure refinement. But the Al–Fe^{2+} disorder, very often assumed in interpretation of MS data, seems to be extremely rare as indicated by the SREF-measured <Z–O> mean bond length and Z site scattering. Additionally, early explanations of MS results provided a simplification in ascribing the Fe^{2+} doublets with quadrupole splitting QS > 2 mm/s to Fe^{2+} at the Y site, and those with QS < 2 mm/s to Fe^{2+} at the Z site. As a result, usually 10–20% and sometimes even 30–50% of total iron was interpreted as the Fe^{2+} at the Z site. Such high amounts of $Fe^{2+}{}_Z$ have never been confirmed by SREF. Therefore, in 1990s investigations focused on finding a new interpretation of Mössbauer spectra on the basis of crystal chemistry of tourmalines

(Kraczka et al. 1986; Pieczka, Kraczka 1994; Pieczka et al. 1998; Kraczka, Pieczka 2001; Gawęda et al. 2002). The model was then positively tested by German and Canadian specialists (simultaneous SREF, MS and IR measurements on the synthetic Fe-Al--tourmaline) and currently forms the commonly accepted basis in interpretation of tourmaline Mössbauer spectra. A coupled X-ray and Mössbauer characteristics of structural changes during oxidation of Fe-tourmalines (Kraczka, Pieczka 2000; Pieczka, Kraczka 2004) also support the Pieczka-Kraczka model and prove (within the error of the method) that Fe^{2+} occupies in tourmalines only the Y site.

GARNETS (*A.P.*)

Garnets have their structure much simpler than that of tourmalines. It is described by the general formula

$$^{[8]}A_3{}^{[6]}B_2\,[^{[4]}TO_4\,]_3$$

where:

A = Mg, Fe^{2+}, Mn^{2+}, Ca,..., B = Al, Fe^{3+}, Cr, V, Ti, ..., and T = Si, Al, Ti, □, (Fe).

Mössbauer investigations of garnets aimed at creation of a similar crystal chemistry model as that described for tourmalines and applicable mainly in detailed interpretation of complex-shaped spectra of the Fe^{3+}- and Ti^{4+}-bearing garnets. The results were inconclusive because of a limited access to such samples (the garnets studied represented mainly Al-bearing varieties) and the garnet project has eventually been abandoned (Pieczka et al. 1996, 1997).

AXINITE (*W.Ż.*)

Axinite is a borosilicate whose very simplified formula is

$$(Ca, Fe, Mn)_3Al_2\,[BSi_4O_{15}\mid OH]$$

In the crystal structure of axinite there exist $[B_2Si_8O_{30}]$ groups, forming nearly planar layers and alternating with the groupings formed by Fe, Al and Ca octahedra. The degree of complication of Mössbauer spectrum depends, as usually, on the number of lattice sites occupied by Fe^{2+} and Fe^{3+} ions. E.g., in the spectrum of the axinite from Strzegom five quadrupoles were detected: two of them correspond to Fe^{2+} in octahedral sites, the next two to Fe^{3+} most probably in both octahedral and tetrahedral sites. Finally, one doublet could result from $Fe^{2.5+}$ mixed valance (delocalization between $^{[6+]}Fe^{2+}$ and $^{[6+]}Fe^{3+}$ ions). More details are given in Pieczka and Kraczka (1994) and Żabiński et al. (2002).

VESUVIANITE (*W.Ż.*)

Vesuvianite is a calcium-aluminium-magnesium ortho-disilicate, containing also some other elements. Its approximate formula can be written as follows:

$$Ca_{19}(Mg, Fe)_3(Al,Fe)_{10}\,[SiO_4\,|\,Si_2O_7\,|\,(O,OH,F)_{10}]$$

In its crystal structure at least ten equivalent cationic sites can be distinguished, five of which can host Fe^{2+} and/or Fe^{3+} ions. Due to such a diversity of iron distribution, this silicate is an interesting object for Mössbauer studies (Kraczka, Żabiński 2003; Karwowski et al. 1996). Six samples, representing both high- and low-temperature varieties of vesuvianites differing in the state of structural ordering, were investigated. It was established that both Fe^{2+} and Fe^{3+} do occupy various lattice sites. In every case, Fe^{2+} dominates over Fe^{3+}. The iron ions, both di- and trivalent, occur mainly in the 6- and 5-coordinated sites, in one case traces of Fe^{2+} were tentatively assigned to the 8-coordinated position.

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