12. ADVANCES IN POWDER DIFFRACTION


Theoretical principles of computer identification of X-ray diffraction powder and spectral data are described with application of database standards. A generalized structure of identification procedure (Hanzawal's strategy) is considered. The conclusion is made that the majority of computer systems of identification (Johnson, Johnson-Vand, Prevel, Snyder, Philips, Siemens, IBM and oth.) have been developed on the basis of some empirical assumptions on a series of searching files and criteria of fitting unknown and standard patterns. The theoretical basis of search/match procedures are based on Plaia's vector form of X-ray diffraction powder patterns representation, on statistical distribution of search signs of standards and on study of crystal chemistry features of database. From an analysis of a mineral subfile distributions of peaks in patterns as regarding their locations and intensities and also distributions of standards due to their crystal chemical parameters were obtained. These distributions allow to establish a value of most informative and significant peaks on patterns, to introduce a compressed handling of spectra the form of binary codes, to prepare an expressed way of investigation of database structure.

As a measure of closeness between unknown and standard patterns it is advisable to use Euclidian distance between these compared spectra in the sign space. All criteria of closeness, which are used in practice (frequency, Johnson-Vand and oth.) could be obtained and ranged by their exactness if these measures could be simplified and different models of line representation could be used.

An investigation of the structure of mineral subfile has allowed to select series of groups of similar patterns and a group of low informative patterns (6-12 peaks in the pattern) for which the probability of casual good coincidence with unknown is higher. It is shown, that the authenticity of identification results depends directly on the structure of database. This appears as a result of computer selection of low informative and of similar standards between true phases. It was stated that similar patterns correspond to standards in which linear lattice parameters differ not more, than by 0.1-0.2Å. Patterns are practically indistinguishable by X-ray diffraction method, if the differences of parameters are of the order of 0.02-0.05Å. This circumstance puts a physical limit of possibilities of the method of qualitative X-ray phase analysis.

A formalization of the method is realized in which information on elementary composition of samples is used. As it is shown, the most informative elements can be pointed out. Numerical criteria of closeness of samples and standards of their chemical composition can be constructed.

12.3.1 THE FLUX GROWTH AND CRYSTALLOGRAPHIC INVESTIGATION OF A NEW COMPOUND, Pb, Bi, Nb₂O₅, IN THE PbO-Bi₂O₃-Nb₂O₅ SYSTEM. By Li Yuyu, Li Deyu, Pu Zhifen and Xu Yuqing. Shanghai Institute of Ceramics, Academia Sinica, China.

According to a method of calculation proposed by Li Deyu et al., the acousto-optical figures of merit of compounds in the PbO-Bi₂O₃-Nb₂O₅ system lie in the range 14-19. These values are comparable with that of PbMoO₄, crystals, widely used in practice. The studies carried out on this system aim at exploring new acousto-optical materials. A new compound composed of 3PbO.Nb₂O₅ and Bi₂O₃ in a molar ratio of 20:1 has been found by using X-ray phase analysis, electron probe and differential thermal analysis. This compound is a congruent one in the PbO-Nb₂O₅-Bi₂O₃, pseudo-binary system. The transparent dark-orange crystals form hexagonal plates when grown by the flux method. The diffraction symmetry determined from transmission Laue and Weissenberg photographs is D₀₃ = 3m. The unit-cell dimensions determined by means of a CAD-4 diffractometer are a = 7.454 Å, b = 9.277 Å. The space-group is P312, P310, P31m, P3m1 or P31m. The indices of strong reflections are consistent with the extinction rule for P3m, P3m1 or P32.

An X-ray powder diffraction pattern was recorded in a Guinier-Hägg focussing camera, diameter 100mm, with highly monochromatic CuKα1 radiation (λ = 1.540598Å). Finely powdered silicon (α = 5.430801Å, 0.335Å at 25°C) was added as an internal standard. Single-coated Shanghai X-ray Fluorescence Film No. 4 was used. Film measurements were made by means of a computer-controlled LS-18 line-scanner. The unit-cell dimensions after refinement by means of the program PIRUM are a = 7.4600(8), b = 9.256(12) Å.

Comparisons between the unit-cell parameters and space-group of this new crystal and those of compounds in the PbO-Nb₂O₅ system lead to the conclusion that the former is a new type of chlorite with a superlattice along the c-axis. The thickness of a sheet in the new type of chlorite structure with superlattice is 3.18 Å. The c-axis of the unit-cell of Pb, Bi, Nb₂O₅ consists of 20 sheets.

Homogeneous and perfect single crystals with sizes up to a = 7.50cm and l = 2cm were grown by the Bridgman method, using the same composition as for the crystals grown by the flux method. An acousto-optical figure of merit M² = 40 was obtained from the observed values n = 2.569 and v(011) = 3x10⁸ m/s. This showed that the crystal Pb, Bi₂, Nb₂O₅ is a potential acousto-optical material.