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Title: **Advanced Computational Analysis of Disordered
Materials and Clay Minerals**

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Project Title: Advanced Computational Analysis of Disordered Materials and Clay Minerals

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Abstract

X-ray and neutron diffraction are the most powerful methods for studying the structures of crystalline solids, including materials of importance to nuclear weapons and environmental programs. Crystallographically disordered solids are some of the most technologically useful materials due to their inherent disorder and high surface areas. Unfortunately, existing crystallographic methods are largely restricted to analyzing ordered materials, and disordered materials cannot be accurately characterized or modeled. We have developed a new method for diffraction analysis of the structural details of disordered materials. The method combines Rietveld refinement methods with a new treatment of disorder that completely describes scattering over all of reciprocal space sampled in a diffraction experiment. This approach has been applied to the common clay minerals but can be equally well applied to other disordered materials, such as zeolite catalysts, superconductors, and nanocomposites, representing a major breakthrough in our abilities to understand the structures of polycrystalline disordered materials.

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL).

Background and Research Objectives

Clay minerals, such as kaolinite, illite, chlorite, and montmorillonite, are among the most common minerals on the Earth's surface. These minerals are composed of layers made up of silicate tetrahedral sheets and Mg, Al, and Fe octahedral sheets. Although the intralayer bonding is dominantly covalent and strong, the bonding between individual layers is very weak, consisting of van der Waals and weak electrostatic interactions. The relatively weak layer-layer interaction energies can lead to considerable disorder in the manner in which individual layers are stacked (a number of solids important to the materials community possess similar characteristics). This weak interlayer bonding leads to a tremendous variety of useful properties, and many different interlayer complexes can be engineered inside such materials. In a sense, the regions between the individual layers can be used as a molecular-

scale chemistry laboratory. These disordered minerals are used in large quantities and are valuable commodities throughout the world. In addition, such minerals are often crucial in determining the characteristics of petroleum reservoir rocks, and clays have been and continue to be the focus of intensive studies by oil companies. Almon and Davies (1981) summarized the importance of clay mineralogy to the petroleum industry by stating "...clay technology is a powerful tool in defining optimum exploration strategies, and should be a vital factor in the planning of efficient well management." Often, the details of the crystal structures and layer stacking of these minerals provide clues to the mode of petroleum formation, migration, and enrichment. Secondary petroleum recovery operations often involve water, steam, or detergent floods. The introduction of these fluids can cause swelling and/or mobilization of clay minerals resulting in losses of permeability sufficient to degrade reservoir quality. It has not been possible to study this process quantitatively because the constituents involved exhibit considerable stacking disorder. Our approach allows convenient and potentially automated analysis of disordered clays, thereby improving the quality of analyses and saving large amounts of money. Petroleum companies spend large amounts of money on detailed analyses of such clay mineral-bearing rocks, and large portions of their research labs are devoted to the study of these minerals.

By far the most common method used to analyze and interpret the mineralogy of clay-bearing rocks is X-ray powder diffraction. Although automated X-ray diffraction instruments have become common in diffraction laboratories in the past ten years, the methods used to *interpret* diffraction data in general and clay mineral diffraction data in particular remain largely unchanged since the 1950's. The typical petroleum company or materials research laboratory still uses qualitative methods to analyze and interpret diffraction data.

Two notable exceptions to this situation exist. The first is the crystal structure refinement and analysis technique known as the Rietveld method. This method was originally developed (Rietveld, 1967, 1969) to refine the structures of crystalline materials using neutron powder diffraction data. Refinement of a crystal structure involves using diffraction observations to improve existing models of the structures of ordered materials. Since then, the method has been modified and used increasingly with X-ray powder

diffraction data, and today this is the most common application of the method. The method has been applied to numerous natural and synthetic materials, most of which do not usually form crystals large enough to study with single-crystal techniques. It is the ability to study the structures of materials for which sufficiently large single crystals do not exist that makes the method so powerful and popular.

Unfortunately, the standard Rietveld method is not applicable to analysis of diffraction data from most clay minerals. An important requirement of this method is that the diffraction data must exhibit *only* Bragg, or three-dimensional (3-D), diffraction effects. Well-ordered materials that yield such diffraction effects have classic reciprocal lattices, where the individual nodes are infinitely small and are not smeared (Fig. 1a). The layered nature of clay mineral structures makes them prone to stacking disorder, giving rise to what are called two-dimensional diffraction effects, *i.e.*, they are partially to completely disordered in the third direction. Such disorder gives rise to significant departures from the classic reciprocal lattice of ordered materials, and the nodes are smeared perpendicular to the direction of disorder (Fig. 1b). Materials that exhibit this type of stacking disorder are also termed “turbostratic.” The disordered nature of their structures makes the application of the standard Rietveld method to clay minerals unwarranted in virtually all cases because the method is incapable of modeling or even approximating the smearing seen in Figure 1b. A similar problem arises from the disordered character of some synthetic zeolites that are used by petroleum companies as catalysts in the production of gasoline from crude oil. Catalytic efficiency is related to the atomic structures of these synthetic minerals, which in turn depend on the synthesis procedures. Crystal structure analysis thus serves as a monitor to guide the experimentalists in their attempts to produce the best catalysts, but the disorder makes traditional powder X-ray diffraction procedures inapplicable. In addition, the amounts and types of disorder confer some of the desirable catalytic properties and require quantification for which, so far, no routine method exists.

The second exception is the recent work of Reynolds (1993) in which he modeled the three-dimensional X-ray diffraction phenomena from disordered crystals. Calculations of intensities of X-rays or neutrons diffracted by a crystal are typically (*e.g.*, in the Rietveld

method) done at each reciprocal lattice node, assuming integral values of the Miller indices (e.g., each node in Fig. 1a). However, in Reynolds' model of intensity diffracted by disordered crystals, the interference function treats the indices of the diffracting planes as *continuous* variables, and diffracted intensity is calculated and summed throughout reciprocal space (e.g., Fig. 1b). Thus, the restriction that diffracted intensity is observed (*and calculated*) only at reciprocal lattice nodes is removed. This method simulates the diffraction of X-rays from disordered structures by calculating the Fourier transform of individual ordered subunits of the structures and by assembling the intergrowth structures in reciprocal space. The contribution from each subunit is summed statistically to form the reciprocal lattice of a "virtual crystal" that is representative of a distribution of crystals with various proportions of each subunit and various ordering states and crystallite sizes. A modification of this methodology was recently used successfully in EES-1 at Los Alamos to model, for the first time, the diffraction phenomena from disordered varieties of silica (SiO₂) known as opal (Guthrie et al., 1995; Bish et al., 2000). In this case, the disordered opal structures were modeled as disordered intergrowths of tridymite-like and cristobalite-like sheets. This research represents perhaps the first applications of Reynolds' statistical Fourier transform summation in reciprocal space to disordered materials other than clays.

Our primary research objective in our research was to integrate the theory and modeling methods used in Prof. Reynolds' research and the work on disordered silica minerals done here at Los Alamos with the methodologies embodied in the standard Rietveld method. Such a crystal structural analysis methodology did not exist previously and is an extremely powerful method for diffraction studies of natural and synthetic materials containing both ordered or disordered materials. Our goal was to implement and test the methodologies to model diffraction phenomena from such materials in a single computer code. The research required development of additional theory of diffraction from disordered materials, implementation of the theory in a modeling code, formulating derivatives for all disorder-related parameters, and testing the code with diffraction data from real disordered materials. Extension of the Rietveld method to disordered structures, with the attendant requirement of summing over all of reciprocal space, was nontrivial and greatly increased computation time. This increase was so great that casual insertion of the existing theory into

the Rietveld algorithm would have produced unacceptable run times on any available computer. Thus a major part of the project consisted of writing and testing very efficient code and taking advantage of all simplifications of the theory that produce errors within acceptable limits for each application. Although the final Rietveld code is not completed, we plan a program with different subroutines, each of which is optimized for a specific application or type of disorder, such as zeolites, micas, silica minerals, kaolinites, etc. Our collaborator at Dartmouth College, Prof. Reynolds, has provided the expertise needed in modeling diffraction phenomena from disordered materials. This research has resulted in the models for each of the specific clay minerals addressed in this report, and all derivatives have been coded to allow insertion into a Rietveld code. With this information in hand, we will finalize a code that embodies the theory of diffraction from both ordered and disordered materials and that can be used to solve a variety of problems in the clay and petroleum industries. We have tested the code on well-characterized and understood model mineral and materials systems, such as micas and the clay mineral kaolinite. This involved measuring accurate X-ray powder diffraction patterns, taking great care to minimize orientation effects. The use of well-characterized materials was important so that the accuracy of the new method could be assessed.

Importance to LANL's Science and Technology Base and National R&D Needs

X-ray and neutron diffraction are the most powerful and often-used methods for evaluating crystalline solids, including essentially all of the solid materials of interest to nuclear weapons and environmental programs in the DOE complex. The methods are used, for example, to study new high-T_c superconductors (*e.g.*, Williams, et al., 1987), the nature of components used in nuclear weapons (*e.g.*, Haschke, et al., 2000), and the nature of natural materials with which chemical and radioactive contaminants interact. Many of these materials are crystallographically disordered, and the quantitative methods available for studying ordered materials are not directly applicable to such disordered materials. Furthermore, the presence of disordered materials in mixtures with ordered materials severely limits the amount of information that can be obtained from the ordered materials. The nanoscience field is an emerging field in which the study of disordered materials is of

fundamental importance, and the methods developed in this research will be directly applicable to many nanomaterials. Although our approach has been applied to the common naturally occurring clay minerals, it can be equally well applied to other disordered materials, such as zeolite catalysts, superconductors, and nanocomposites, representing a major breakthrough in our abilities to understand the structures of such polycrystalline disordered materials.

This new methodology is directly applicable to problems in the clay, zeolite, and petroleum industries, and we have established specific collaborations with several clay and petroleum companies to use their materials as test samples. For example, ECC International is concerned with determining directly and automatically the degree of disorder in kaolinite samples that they use as fillers, adsorbants, and coatings. ECC researchers have previously established relationships between kaolinite disorder and the performance of kaolinites as coatings and pigments, but structural characterization of their kaolinites is tedious, inaccurate, and cannot presently be automated. Likewise, petroleum companies will be able to implement the automated Rietveld quantitative analysis techniques, partially developed at Los Alamos (*e.g.*, Bish and Howard, 1988), with oil reservoir samples containing partially ordered clay minerals. Several superconducting materials have layer structures like the clay minerals, and some show the same types of disorder. We will therefore continue to communicate and collaborate with researchers in this field to apply our new methods to layered superconductors and nanocomposites. In addition, this code is germane to collaborations involving zeolites being pursued under the UCSB-Los Alamos Frontiers Of Materials Science Program.

Scientific Approach and Accomplishments

The Rietveld method is a least-squares procedure in which the entire powder diffraction profile (obtained either with neutrons or X-rays) is modeled as a sum of contributions from Bragg reflections (reflections from individual lattice planes in the crystal) and background. Bragg scattering for ordered materials occurs only in small regions of reciprocal space (ideally delta functions or infinitely small points, *e.g.*, Figure 1a) and the

summation is greatly abbreviated by calculating intensity contributions only at each theoretical Bragg reflection and applying an analytical profile broadening function (*e.g.*, a Gaussian) over a short 2θ range about this position. The Rietveld refinement model for a normal powder diffraction pattern has adjustable coefficients that describe the crystal structure (atom positions, etc.), peak positions (unit-cell parameters, etc.) and peak shapes (mathematical profile coefficients, etc.). The model can also include other effects such as absorption and texture (preferred orientation). The background is fit with a semi-empirical function as part of the refinement. A typical fit for a mixture of two crystalline, well-ordered phases is shown in Figure 2. Note that the peaks are symmetric and occur in well-defined locations indicated by the pairs of reflection markers at the bottom of the figure. In the case of disordered or partially ordered materials, however, scattering occurs over much wider regions of reciprocal space and thus the simplification in the summation procedure for the Rietveld method is no longer applicable. Figure 3 shows a diffraction pattern of a disordered clay mineral, illustrating the asymmetric, so-called two-dimensional diffraction bands characteristic of disordered layer-structure materials. To model the diffraction patterns of such disordered materials correctly, a complete description must be made of the scattering over all parts of reciprocal space sampled in the diffraction experiment (*e.g.*, Figure 1b). This can be achieved by correctly modeling the statistical distributions of different structure types in the “virtual crystal.” Therefore, the calculation of intensity diffracted by a disordered crystal involves independently calculating the intensity at *every* measured 2θ step in a digital powder diffraction pattern rather than only at the reciprocal lattice nodes, a major coding and computational undertaking. Such a calculation can be several orders of magnitude slower than a traditional Rietveld calculation. Therefore, a refinement procedure based on this type of model, in contrast to the standard Rietveld method, requires a much-simplified parameter set that is largely focused on those that characterize the disordered material. These parameters describe the microstructures characteristic of the disordered material (*e.g.*, types of layer, degree of disorder, type of disorder, size of coherent domains, interlayer spacing, etc.), thereby providing important quantitative information. Although the term “layer” is used here, it is meant only to connote a discrete structural unit, and the methods developed are not restricted to layer materials. Attempts have been made in the literature to model such disordered materials using the conventional Rietveld method. However, such calculations in

no way simulate the true diffraction effects and almost always lead to erroneous results. Furthermore, such simplifications provide no information on the type and degree of disorder. For example, Figure 4 compares the observed diffraction pattern of an ordered kaolinite with that of a completely disordered kaolinite having the same structure within each layer as the ordered material. It is obvious that simple broadening of the reasonably sharp peaks will not result in the diffraction pattern of the disordered material. Only a calculation that considers much or all of reciprocal space can simulate the diffraction patterns of such materials.

To date we have used the fastest available personal computers to implement the modeling methodology, but the final code will probably require faster Los Alamos computers. Simple structure refinements that incorporate the full disorder code would require more than 24 hours of computer time on the fastest available personal computers. We have also done preliminary implementation of the disorder code in the Rietveld method, using our Rietveld codes as a basis. Initial tests and improvements were done using reasonably well-characterized model compounds such as kaolinites and micas. Figure 5 compares simulations of a completely ordered and a disordered mica; the code accurately simulates the form of the two-dimensional diffraction bands found in the patterns of disordered micas. Figure 6 shows a similar comparison of simulations for micas with differing degrees of disorder. This figure illustrates that it is possible to obtain very detailed information on the types of order present in layered materials and to discriminate between similar types of disorder. Such analyses and discrimination has heretofore been impossible. We have also theoretically analyzed the effects of random displacements between the layers of clay minerals. Figure 7 compares the diffraction pattern of a well-ordered kaolinite with the pattern for the same material having random 1 Å displacements between layers in the X-Y plane. Note the development of two-dimensional diffraction effects in the pattern of the material with random layer displacements. Similar types of layer displacements can be artificially induced during sample preparation or grinding. These figures illustrate that this new modeling methodology has successfully simulated the diffraction patterns of a variety of disordered clay minerals, including kaolin minerals, illite/smectites, and chlorites. For most materials, these first-principles simulations model even subtle variations in X-ray powder diffraction patterns. Because these simulations involve explicit calculation of the entire

intensity distribution at every 2θ step, it will be reasonably straightforward to incorporate these models into the Rietveld method.

For further testing, we will collect high-quality X-ray and neutron diffraction data from disordered materials in our laboratories. In addition, we again have expressions of interest from several petroleum and clay companies, and we envision using some of their samples to test our newly developed methods in the future. It is clear from letters (included with the original proposal) sent by industry representatives that they believe such a new methodology is of great importance to them, improving their productivity and global competitiveness. We expect that our results will lead to an extremely powerful computer code that can model the diffraction effects from both ordered and disordered materials of virtually any type. Such a code will be revolutionary in its ability to treat and analyze diffraction data from a variety of multicomponent materials. Although we have primarily targeted the area of clay mineralogy for an important application of this methodology, the new code will be equally applicable to the materials industry wherever disordered materials are important, such as with zeolite catalysts, nanocomposites, C-based intercalation compounds, high-Tc superconductors, $\text{FeF}_2/\text{ZnF}_2$ and GaAs/AlAs superlattices, and multilayer crystals. No such code is presently available, and we believe it is safe to say that development of a working code will be a major milestone in diffraction studies. We believe the new combined method represents a breakthrough in our abilities to analyze the structures of polycrystalline disordered materials, a breakthrough that could well be similar in magnitude to that represented by the standard Rietveld method.

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Figures

- Figure 1. Schematic reciprocal lattice (a) for a three-dimensionally ordered material and (b) for a turbostratically stacked layered material with stacking disorder along c^* . Note that the reciprocal lattice nodes in (a) are points, whereas these nodes have degenerated to rods in (b) that are perpendicular to the layers (or parallel to the stacking direction).
- Figure 2. Observed (plus symbols, +) and calculated (overlapping solid curve) diffraction patterns for a mixture of two crystalline, well-ordered phases resulting from a typical Rietveld refinement. The “difference pattern” represents the calculated minus the observed pattern, and “reflection markers” show the calculated positions of Bragg reflections. They exist in pairs because the X-ray tube used (Cu) produces two similar wavelengths.
- Figure 3. X-ray diffraction pattern of a typical smectite clay (completely disordered), showing both “Bragg” basal reflections and the asymmetric, so-called two-dimensional diffraction bands that cannot be modeled using the Rietveld method.
- Figure 4. Comparison of the observed diffraction pattern of an ordered kaolinite with that of a completely disordered kaolinite. The pattern of the disordered kaolinite consists of both Bragg reflections and two-dimensional diffraction bands. The two-dimensional bands cannot be approximated by broadening of the Bragg reflections seen in the pattern of the ordered kaolinite.
- Figure 5. Comparison of simulations of a completely ordered (1M trans) and a disordered (turbostratic) mica; the code accurately simulates the form of the two-dimensional diffraction bands found in the patterns of disordered micas.
- Figure 6. Comparison of simulations for micas with differing degrees of disorder including: a) a mica with a 0.667 probability of having 120° rotations of adjacent layers; b) a mica with a 0.3 probability of having 120° rotations of adjacent layers; and c) a mica that is 50% turbostratic (disordered). Note that it is straightforward to distinguish between a) and b).
- Figure 7. Comparison of the diffraction pattern of a well-ordered kaolinite with the pattern for the same material having random 1\AA displacements between layers in the X-Y direction (within the layer plane).

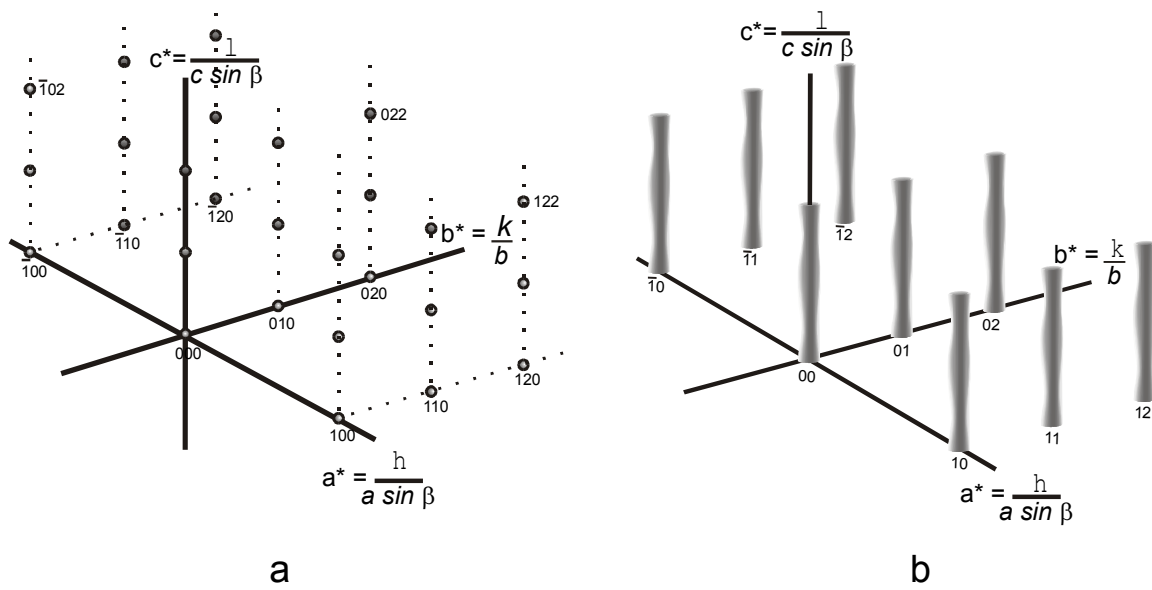


Figure 1

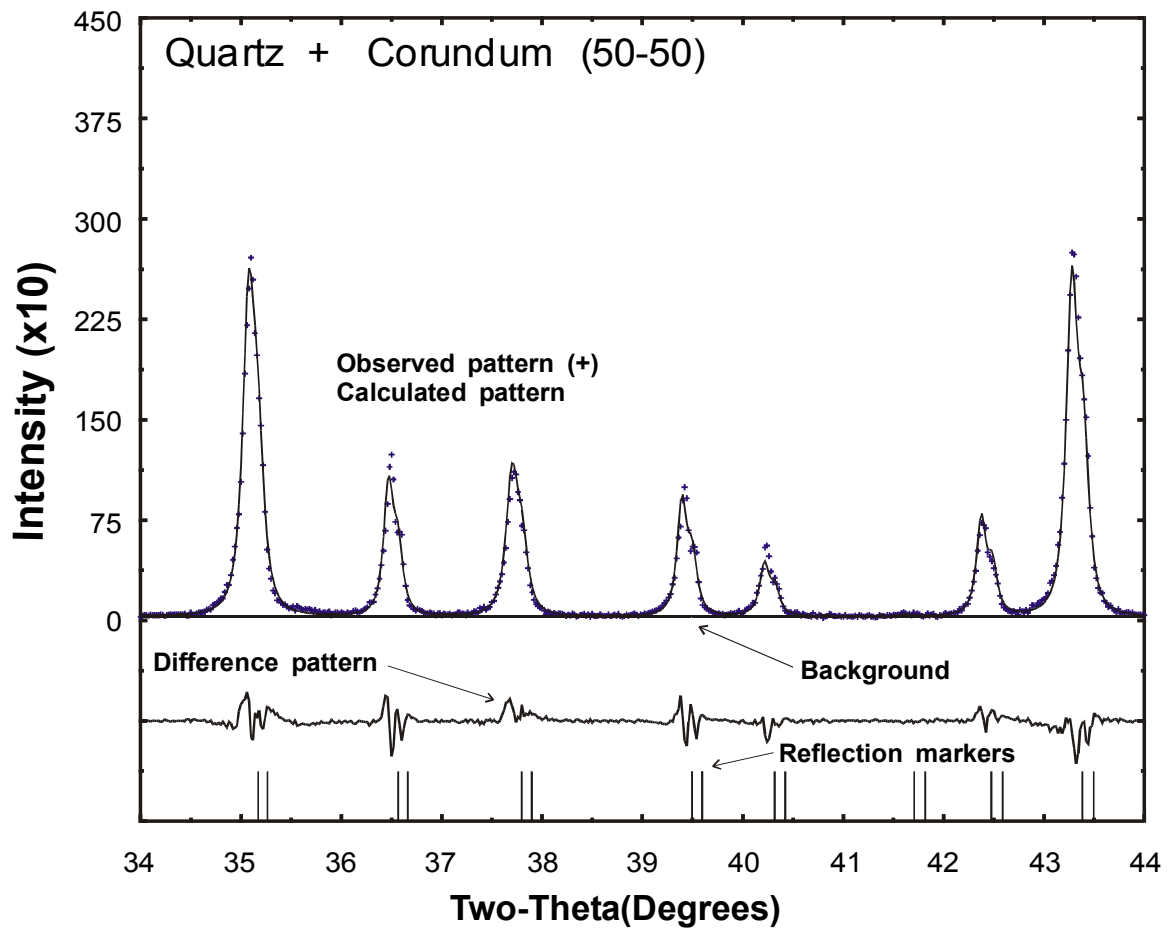


Figure 2

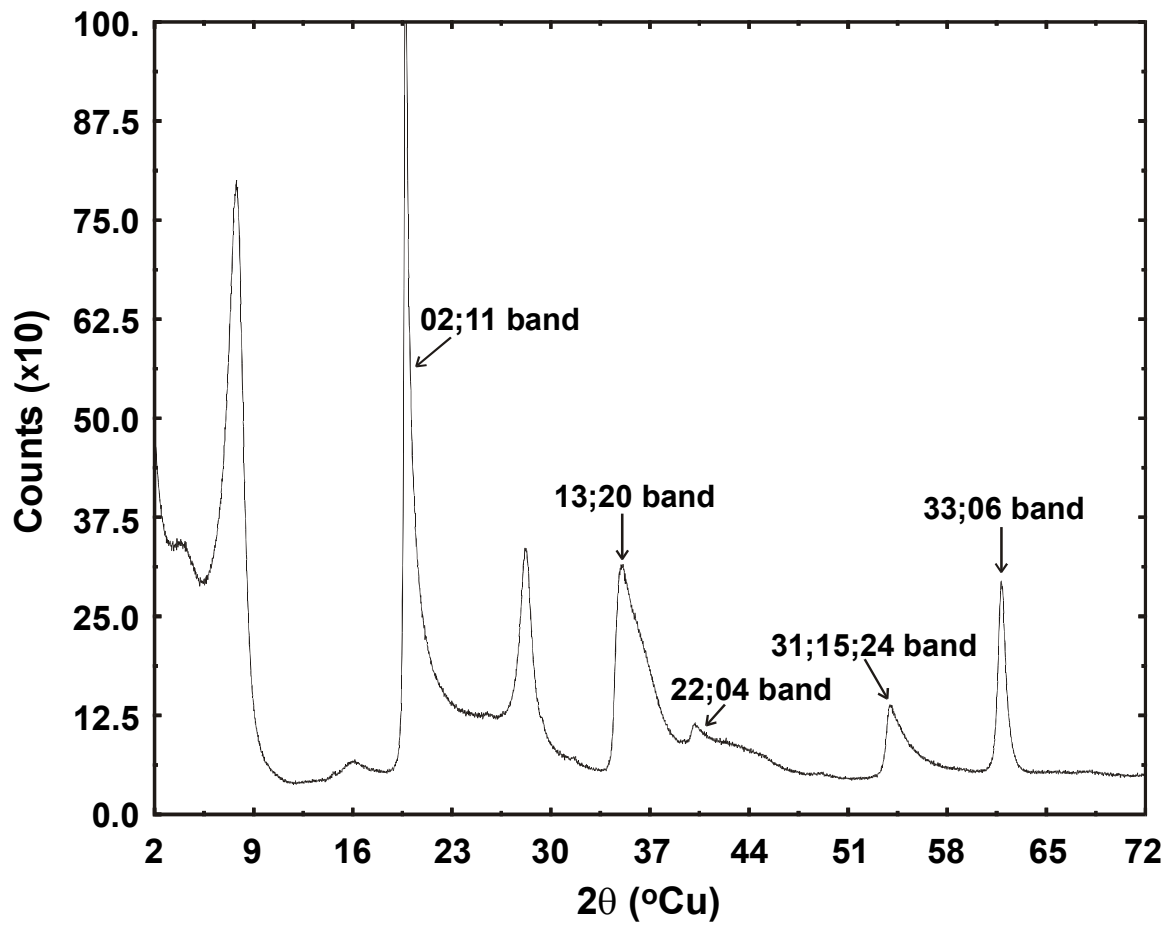


Figure 3

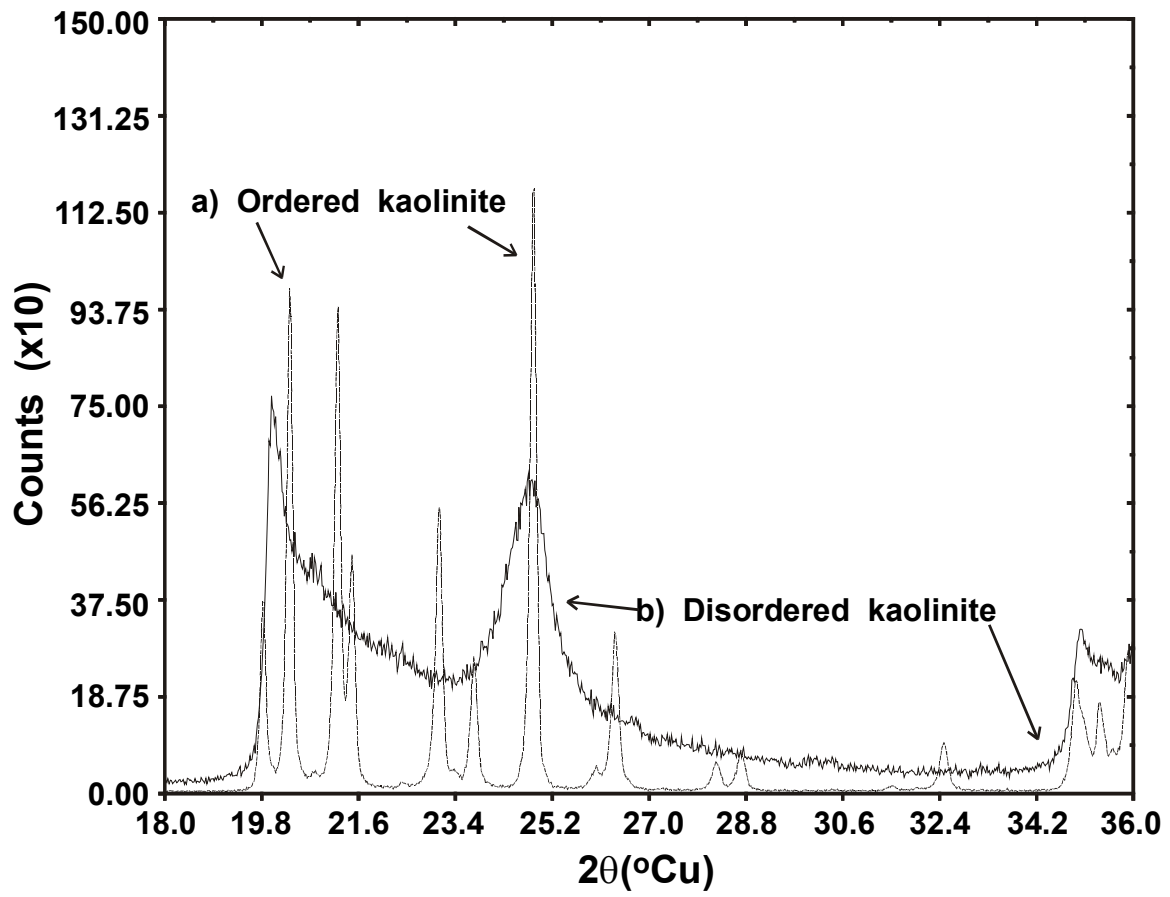


Figure 4

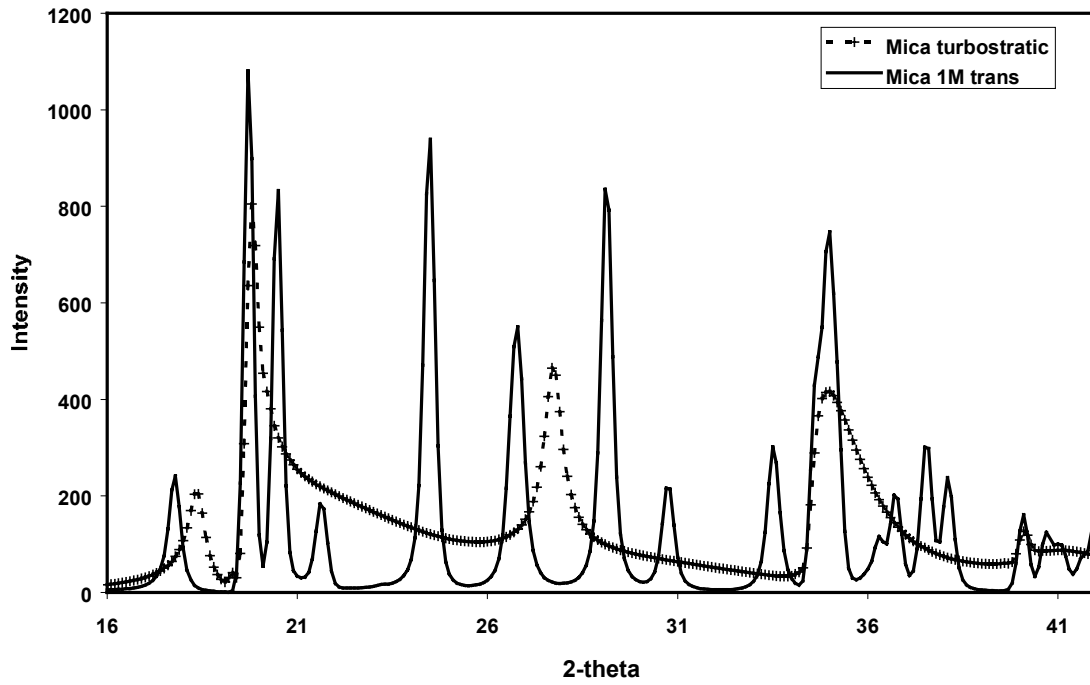


Figure 5

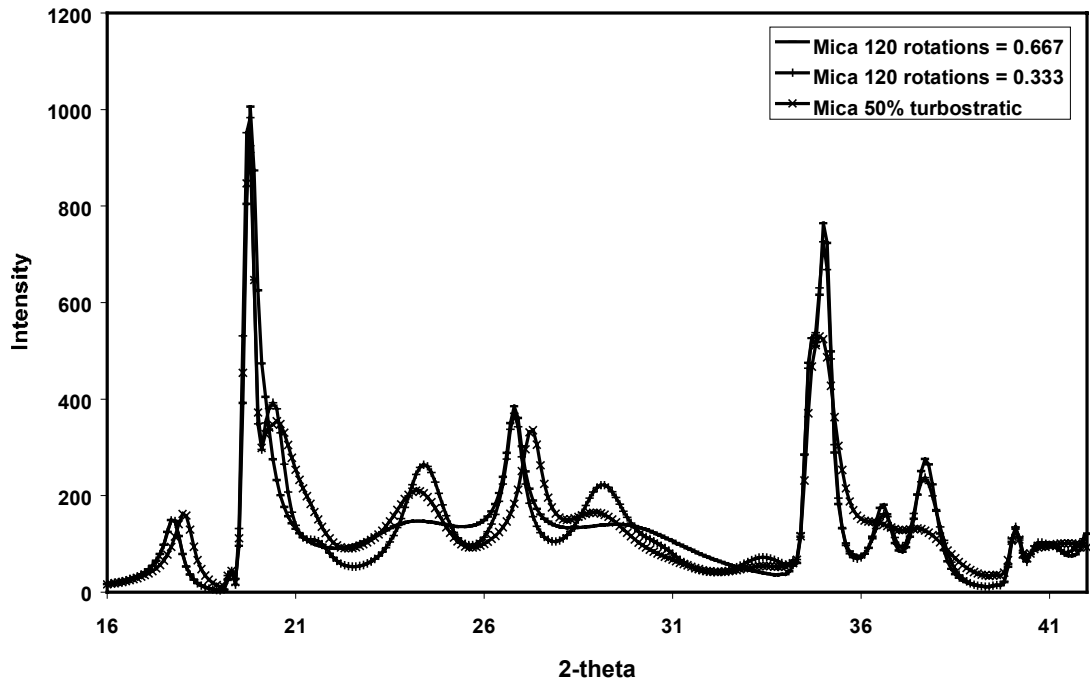


Figure 6

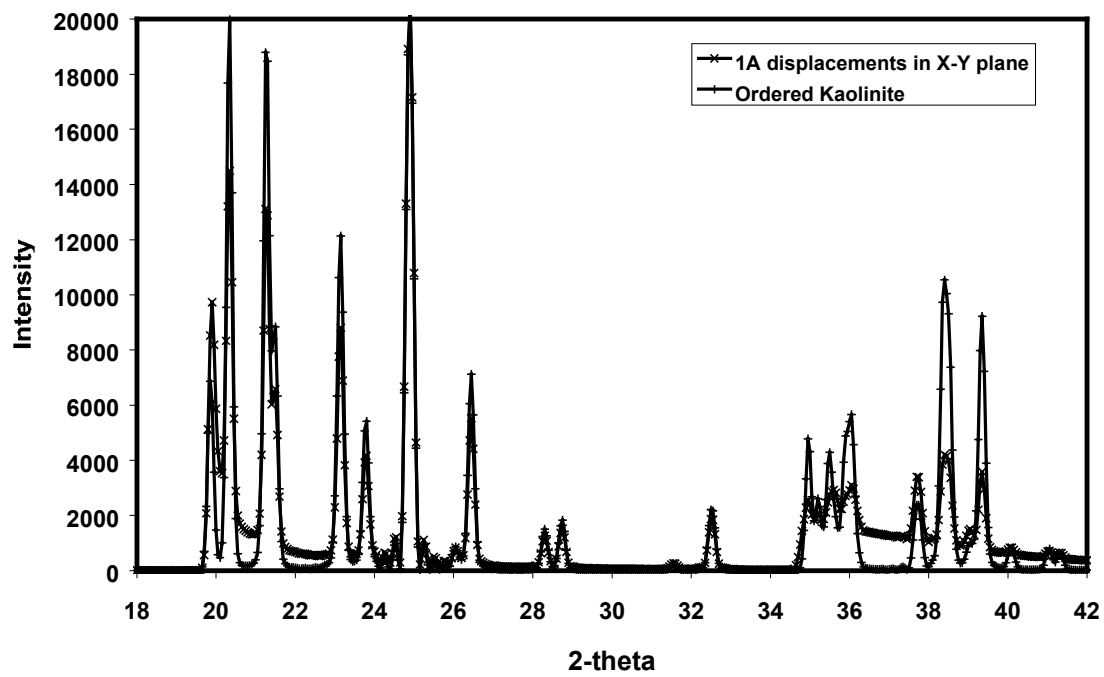


Figure 7