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<UNIDO Project TF/GLO/95/005>

WORKSHOP
ON
THE MEASUREMENT ACCURACY OF X-RAY POWDER DIFFRACTION

November 19 ~ 22, 2002

Submitted by Dr. Hyun Min PARK
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한국표준과학연구원
KOREA RESEARCH INSTITUTE OF STANDARDS AND SCIENCE

1. Introduction

The X-ray powder diffraction method has been used to obtain structural and micro-structural information of materials and their quantitative analysis through powder diffraction patterns. The method is also widely applied not only to the material sciences, but also chemistry, geology, physics, medical sciences, etc.

With the unprecedented pace of development of new materials in recent years, there has been a rapid increase in demand of the materials industries for precise analysis of X-ray powder diffraction. As a matter of fact, what the industry requires is reliable analysis data of the X-ray powder diffraction, which is based on the results of mutual comparisons between laboratories. Being crucial for the development of new materials and their efficient incorporation into competitive and environmental-friendly industrial products, the reliability depends on the standardized method of analysis at the laboratories.

Therefore, it is very important to develop standardized measurement procedures and data reduction process for mutual comparison between data obtained by different analysis equipment in different countries. It is true that such efforts have been made independently by some of the developed countries, but there exists no unit in the international community to coordinate all the related activities. Even in the International Organization for Standardization (ISO), most of the related activities are scattered in many Technical Committees, which makes it difficult to develop standardized measurement procedures in this particular field. Therefore, it is necessary to establish an ISO TC dealing with the X-ray measurement.

The workshop has been conceived to provide a basis for multilateral cooperative activities in the area of X-ray powder diffraction analysis which will contribute to establishing an ISO TC in this area. The workshop is also expected to help enhance technical capabilities of the participating countries in the quantitative and qualitative analysis and measurement of X-ray diffraction XRD.

The work program of the UNIDO International Center for Materials Evaluation Technology (ICMET) includes the assistance to the developing countries in

frontier scientific and engineering research and training in these areas. The workshop, having been organized as part of the ICMET program by the KRISS Division of Chemical Metrology and Materials Evaluation from November 19 ~ 22, 2002, will therefore be beneficial particularly for the developing countries and vital for their sustainable industrial and economic development.

2. Participants List

Country	Participants (including contact details)
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3. Instructors

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4. Workshop Program *(Some photographs taken during the schedule are attached in Annex A.)*

Nov. 19 (Thu)

09:00 ~ 09:10 Opening Remarks
Dr. Yang Koo Cho, President of Korean Crystallographic Association/Director, Division of Chemical Metrology and Materials Evaluation, KRISS

09:10 ~ 09:30 Introduction to APEC Project: Background and Future Plan, Dr. Gun Woong Bahng, Project Overseer, KRISS

09:30 ~ 10:30 *"Accuracy in X-ray powder diffractometry"* by Prof. Robert Snyder, The Ohio State University, USA

10:30 ~ 11:00 Break

11:00 ~ 12:00 *"To solve structures from powder diffraction, first they must be indexed!"* by Dr. Lachlan M. D. Cranswick, School of Crystallography, Birkbeck University of London, U.K.

12:00 ~ 13:30 Lunch

13:30 ~ 15:30 *"Structure determination and Rietveld refinement using powder diffraction data"* by Prof. Hideo Toraya, Ceramics Research Laboratory, Nagoya Institute of Technology, Japan

15:30 ~ 15:50 Break

15:50 ~ 16:10 Introduction of KRISS (by Slide Film)

16:10 ~ 17:00 Lab Visit (Materials Evaluation Center), Dr. Hyun Min Park, KRISS

- 18:30 ~ Welcome Dinner

Nov. 20 (Wed)

09:00 ~ 10:00 *"Introduction to the HANARO neutron facilities"* by Dr. Yong Nam Choi, HANARO Center, Korea Atomic Energy Research Institute (KAERI), Korea

10:00 ~ 11:00 *"Fundamentals of quantitative analysis"* by Prof. Robert Snyder, The Ohio State University, USA

11:00 ~ 11:30 Break

11:30 ~ 12:30 *"The CCP14 Project - freely available crystallographic and powder diffraction software for scientific research and quality control"* by Dr. Lachlan M. D. Cranswick, School of Crystallography, Birkbeck University of London, U.K.

12:30 ~ 14:00 Lunch

14:00 ~ 16:00 *"Aspect of accuracy in the application of X-ray and neutron diffraction techniques to ceramics and catalysts"* by Dr. Burkhard Peplinski, Chemical Analysis Division, Federal Institute for Materials Research and Testing (BAM), Germany

16:00 ~ 16:30	Break
16:30 ~ 17:30	*"Some tricks and hints for using Alan Larson and Bob von Dreele's GSAS and Brian Toby's EXPGUI for Rietveld crystal structure refinement of minerals and polymeric inorganics from powder diffraction data"* by Dr. Lachlan M. D. Cranswick, School of Crystallography, Birkbeck University of London, U.K.

Nov. 21 (Thur)

09:00 ~ 11:00	"*An overview of NIST SRMs for Powder Diffraction*" by Dr. James P. Cline, Ceramics Division, National Institute of Standards and Technology (NIST), USA
11:00 ~ 11:30	Break
11:30 ~ 12:30	*"X-ray diffraction in crystals with planar defects, 1) cubic crystals with stacking faults"* by Dr. Anatolii Ustinov, International Center for Electron Beam Technologies, Kiev, Ukraine
12:30 ~ 14:00	Lunch
14:00 ~ 15:00	"*X-ray diffraction in crystals with planar defects, 2) Tetragonal crystals with twin walls"* by Dr. Anatolii Ustinov, International Center for Electron Beam Technologies, Kiev, Ukraine
15:00 ~ 16:00	"*Rietveld refinement of* $BaMgAl_{10}O_{17}:Eu^{2+}$ *using X-ray and Neutron Powder Diffraction Data*" by Dr. Yong Il Kim, KRISS, Korea
16:00 ~ 16:30	Break
16:30 ~ 17:30	Wrap up Discussion

Nov. 22 (Fri)

09:00 ~ 10:30	Visit to Korea Atomic Energy Research Institute (KAERI)
12:30 ~ 18:00	Lunch and Seoul Tour
18:00 ~ 20:00	Dinner and Check in at a Hotel in Seoul (Sofitel Ambassador)

5. Summary of Lectures

Accuracy in X-ray powder diffractometry

The lecture was focused mainly on the familiarization of the participants to the techniques of XRD. The origin of X ray powder diffraction was reviewed, and the geometry of the instrumentation was explained in details. In addition, there was a lecture about the factors effecting on the X-ray powder diffraction data, and also the basic ideas of XRD data analysis and interpretation through representative examples commonly encountered in practical analysis method which is involved in data reduction procedure, calibration procedures, and assessing data quality and accuracy.

To solve structures from powder diffraction, first they must be indexed!

The lecture was focused mainly on the followings.

- Some history of Indexing of Powder Diffraction Data
- Peak finding and peak profiling software
- Fundamental Parameters Peak Fitting
- Available powder indexing software and indexing suites
- Crysfire in action
- Chekcell in action
- Mmap with Crysfire 2002 (released August 2002)
- MCMaille by Armel Le Bail (released Sep 2002)
- Possibilities for the future and conclusion

Structure determination and Rietveld refinement using powder diffraction data

The lectures were focused on the explanation of direct method to apply the structure determination and Rietveld refinement using powder diffraction data, as well as on the introduction of accuracy of structural parameters in Rietveld refinement and weight function such as Rietveld refinement of a-Si_3N_4.

Introduction to the HANARO neutron facilities

Overview of HANARO neutron facility was made. The neutron diffraction is used to the structure analysis as complementary tools. Various applications used to structure analysis were given in details.

Fundamentals of quantitative analysis

It was explained about the quantitative analysis by X-ray diffraction. The main topics include:

- Vegard's Law Analysis;
- Spiking or Method of Standard Additions;
- Absorption Diffraction Method;
- Internal Standard Method;
- I/Ic and the RIR;
- The Generalized RIR Method;
- Normalized or "Standardless" Analysis; and
- Whole Pattern Fitting and Rietveld Analysis.

The CCP14 Project - freely available crystallographic and powder diffraction software for scientific research and quality control

There was an explanation about the CCP14 project which is connected with a freely available crystallographic and powder diffraction software for scientific research and quality control. Introduction was also made to the trainee about "crystallography suites that link directly into the crystal structure databases". The structure analysis procedures were given in the following,

- Peak profiling
- Unit Cell refinement
- Powder indexing
- Structure Solution
- Structure refinement
- Structure validation

- Photorealistic rendering of crystal structures

Aspect of accuracy in the application of X-ray and neutron diffraction techniques to ceramics and catalysts

The contents of the lecture consist of two parts. One is about the application of Rietveld method for accurate quantitative phase analysis based on CRM BAM-S001 silicon nitride powder, and the other is about the XRPD under ambient conditions tools and examples of application of an XRK which is used for industrial catalysts, fuel cell, hydrogen storage materials, oxygen separation membranes, etc.

Some tricks and hints for using Alan Larson and Bob von Dreele's GSAS and Brian Toby's EXPGUI for Rietveld crystal structure refinement of minerals and polymeric inorganics from powder diffraction data

Information was provided about on how to perform restrained Rietveld refinement of large inorganics using GSAS including:

- Data conversion
- Histogram weighting
- Charge Balance Restraints
- Total cell composition restraints
- Bond length restraints
- Bond angle restraints
- Using Platon and WinGX to help validate the structure

An overview of NIST SRMs for Powder Diffraction

The lecture was focused mainly on the overview of NIST SRMs for powder diffraction. The lecture also dealt with X-ray powder diffractometer such as principal instrumental aberrations, aligned diffractometer, profile position and shape parameter, instrumental configuration and procedures, quantitative analysis, etc.

X-ray diffraction in crystals with planar defects, 1) cubic crystals with stacking faults and 2) Tetragonal crystals with twin walls

The emphasis was put on the special X-ray diffraction technique which can be applied to the stacking fault analysis. Through the comparison with the simulation and real XRD pattern, the analysis of the stacking fault in Cu powder was presented. The tetragonal crystals with twin walls was also treated.

Rietveld refinement of $BaMgAl_{10}O_{17}$: Eu^{2+} using X-ray and Neutron Powder Diffraction Data

An example was presented about Rietvel refinement on the $BaMgAl_{10}O_{17}:Eu^{2+}M$ which is used for the PDP materials. More precise structural parameters for $BaMgAl_{10}O_{17}:Eu^{2+}$, such as lattice parameters, the site preference of Mg, site fractions of Mg and Eu, etc. were determined by the combined Rietveld refinement using X-ray and neutron powder diffraction data.

6. Conclusion

X-ray powder diffraction methods have been used to examine the crystalline structures of material during the last decades. In the late 60s, for example, Rietveld method became a powerful tool in X-ray diffraction technique and it was introduced to analyze the crystal structure. Although X ray powder method is simple, however, it is very difficult to obtain the precise data because of the various sources of error.

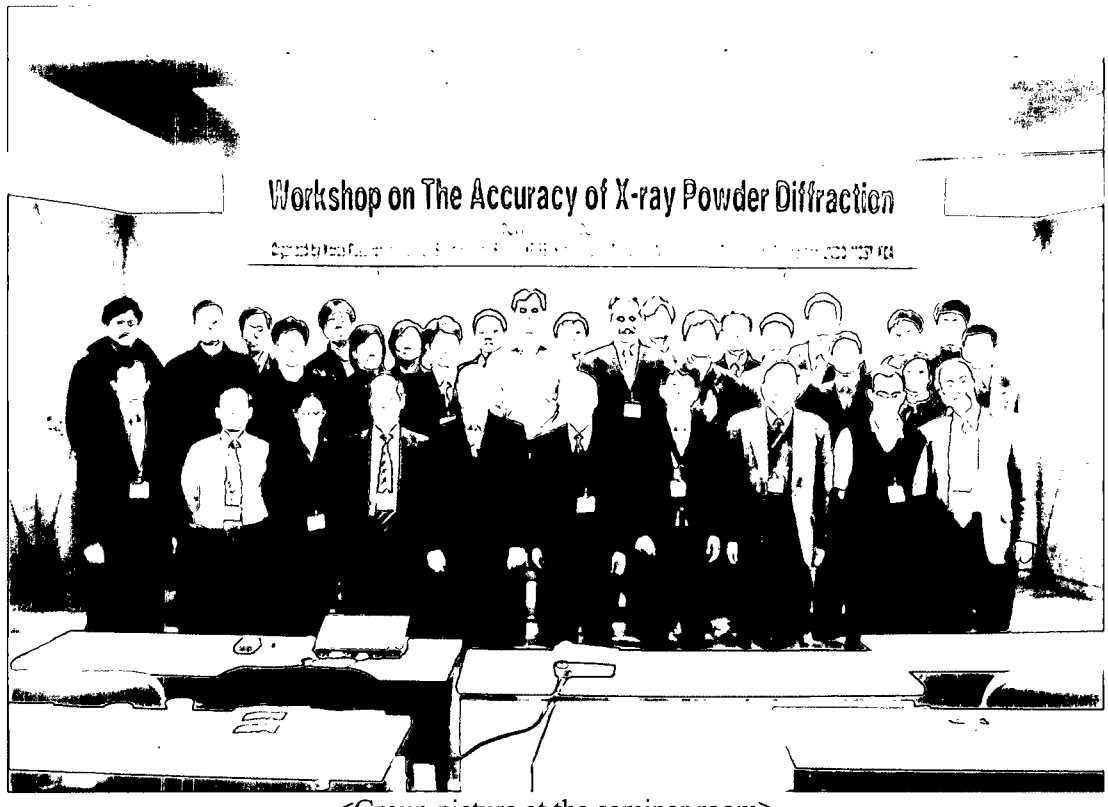
The workshop was intended to emphasize the importance of accuracy in X-ray powder diffraction as well as quantitative analysis.

All the participants showed much interest especially in the lectures and hands-on sessions on quantitative analysis and software programming used for structure analysis. In order to enhance technical capabilities of the participating countries in the quantitative and qualitative analysis and measurement of X-ray diffraction XRD, it was agreed to perform a Round Robin Test (RRT) about the quantitative analysis of the polymorphic phase such as α/β Si_3N_4 in the coming 2003.

Annex I. Photographs taken during the workshop

Annex II. Workshop leaflet

Annex A. Photographs taken during the workshop



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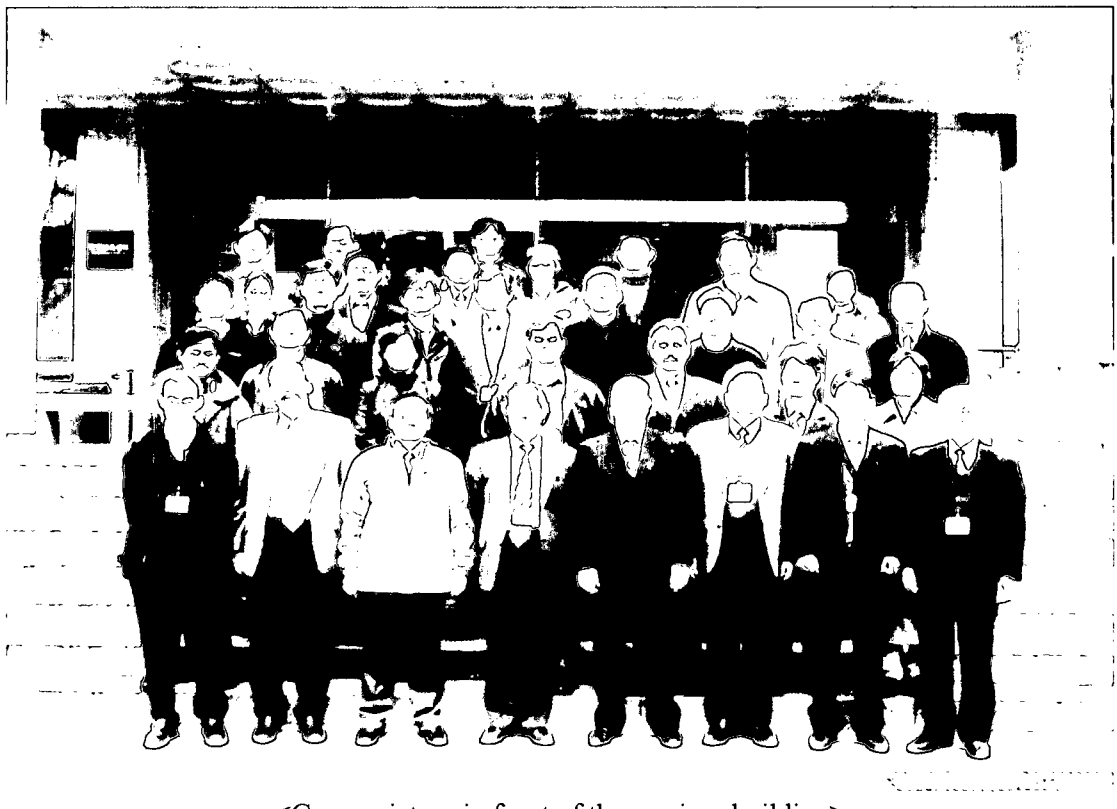

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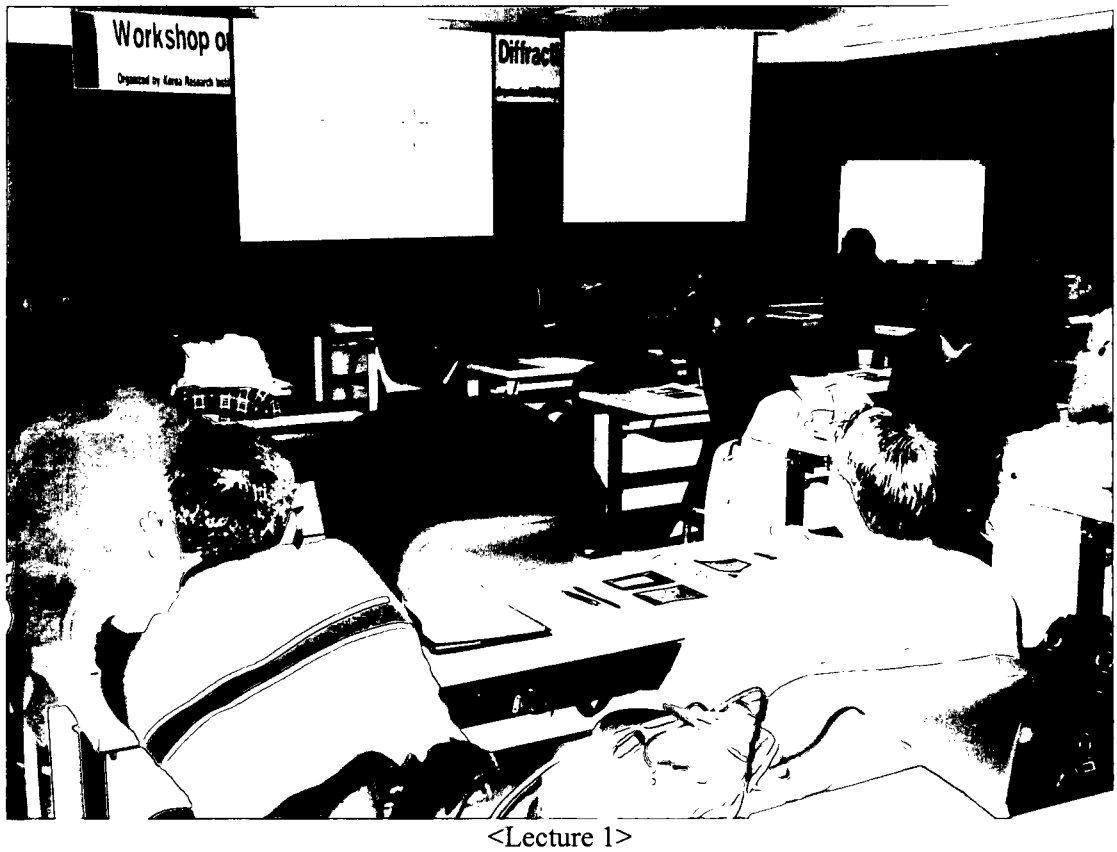

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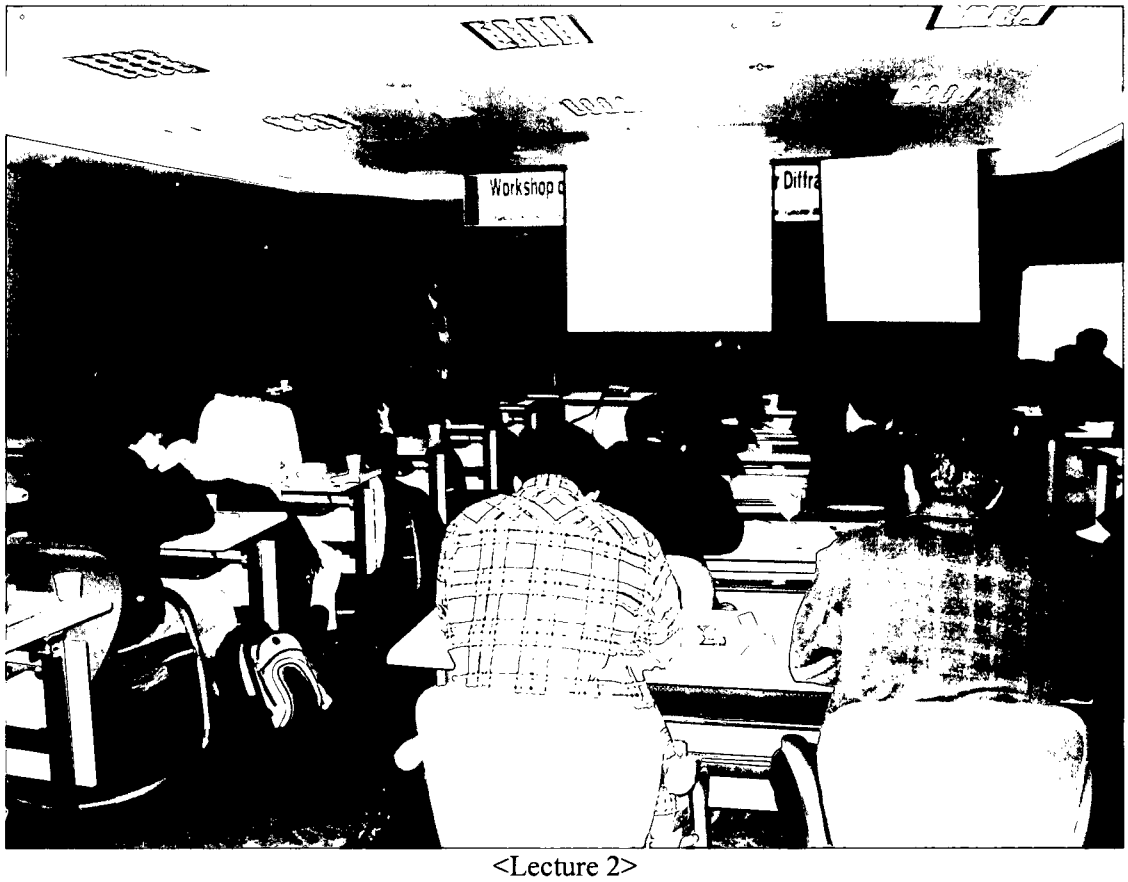

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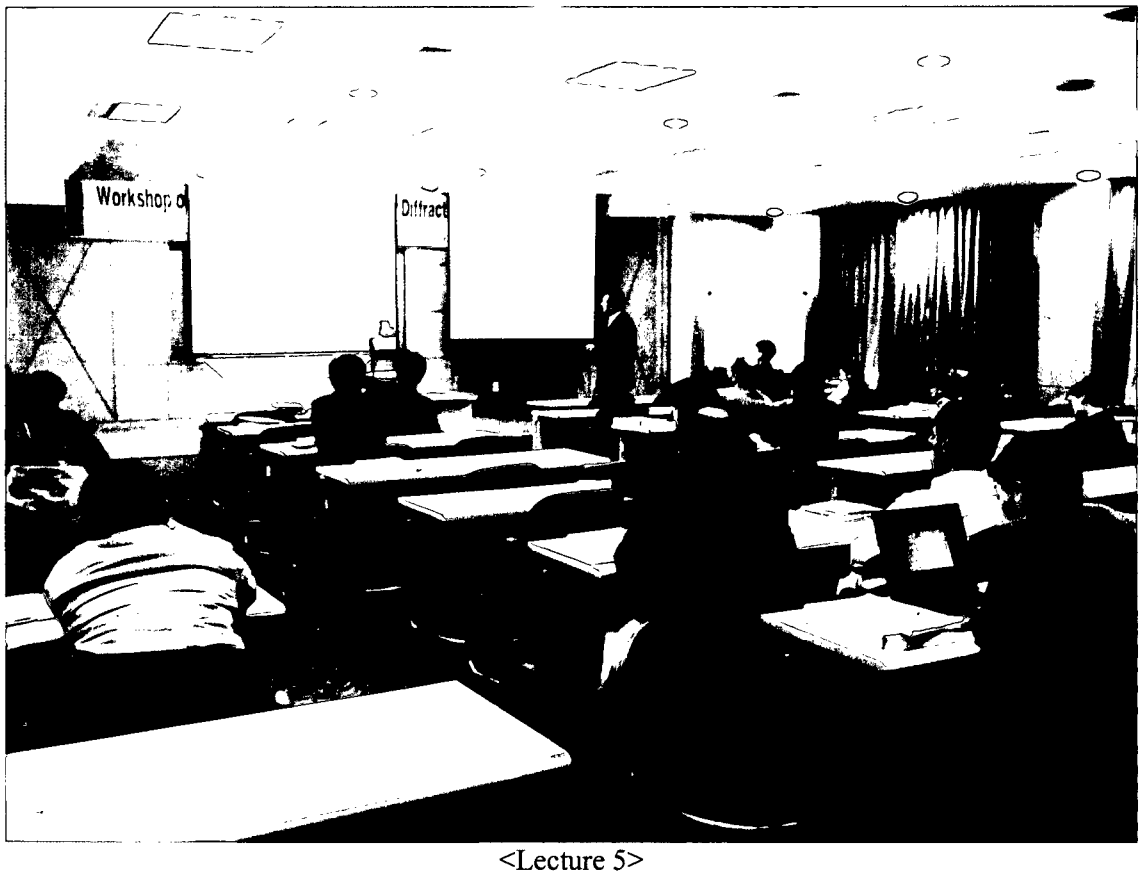

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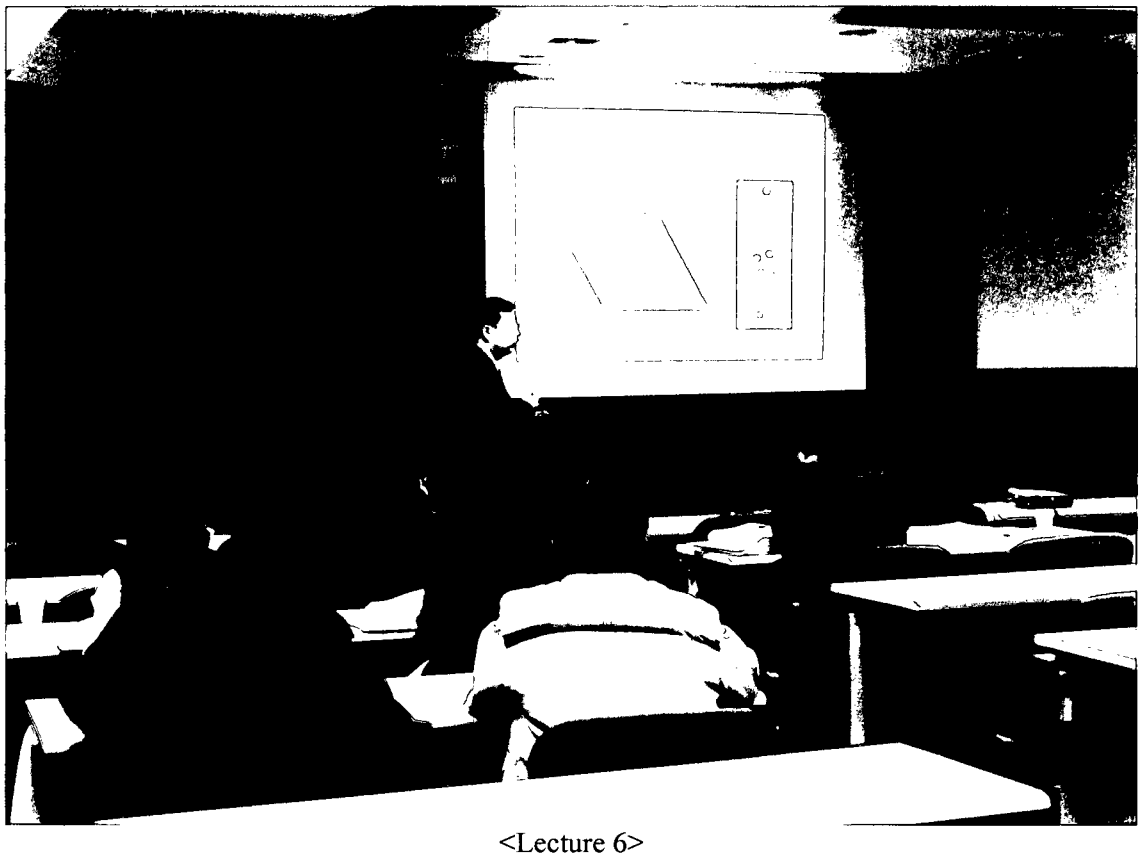

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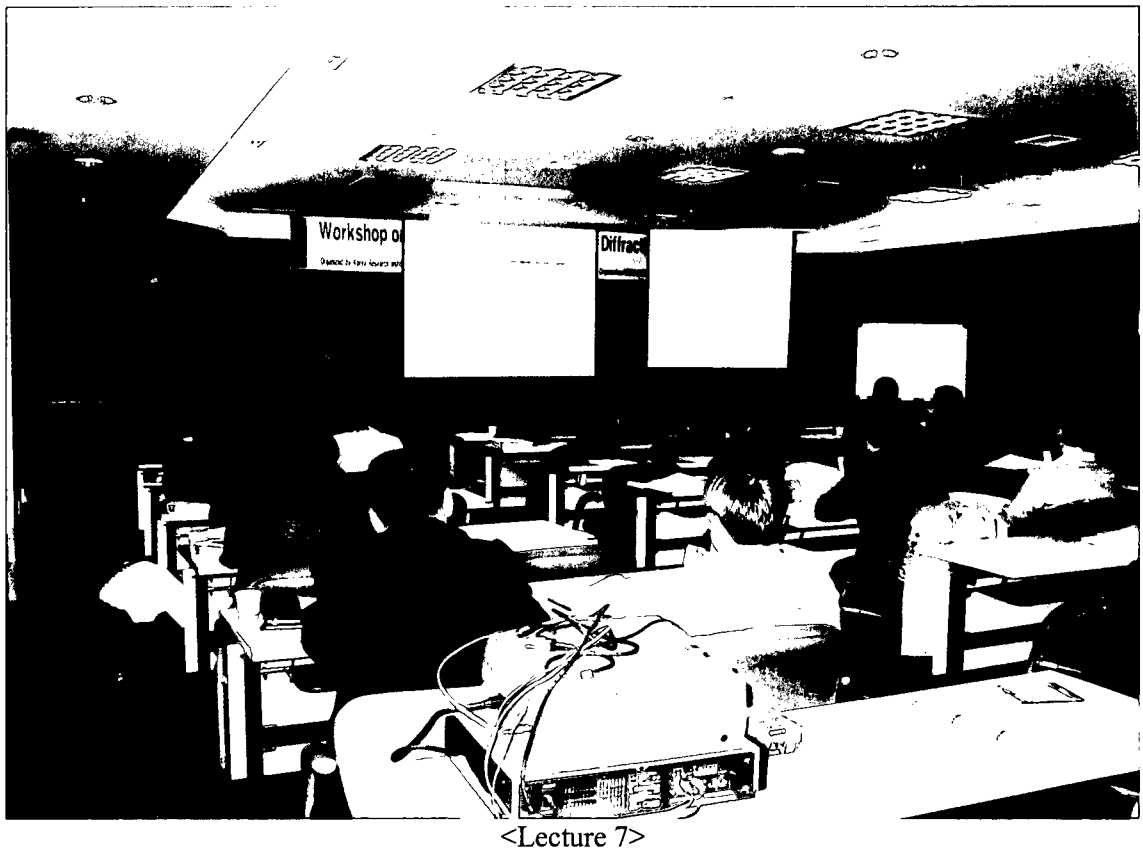

<Lecture 7>


<Dinner 1>

<Dinner 2>

진행 순서

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09:00~11:00 *"An overview of NIST SRMs for Powder Diffraction"* by Dr. James P. Cline, Ceramics Division, National Institute of Standards and Technology (NIST), USA

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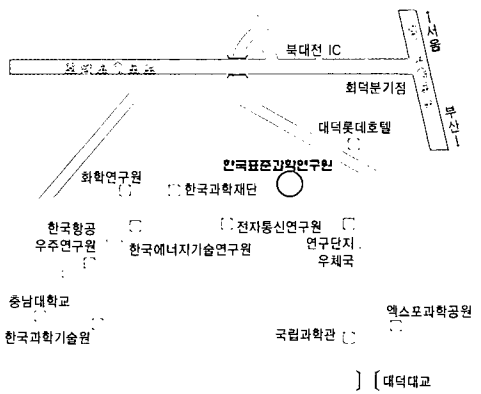
Nov. 22 (Fri)

08:30~10:30 Move to Suwon
10:30~12:00 Visit to SamSung Co.
12:00~18:00 Seoul Tour
18:00~20:00 Dinner (Korea House)
20:00 Check in at a Hotel in Seoul (Sofitel Ambassador Hotel)

Nov. 23 (Sat)

Departure

오시는 길



○ 승용차

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○ 고속버스

유성고속버스터미널(택시이용 3천원정도, 10분거리)
대전(동부)시외버스터미널(택시이용 5천원정도, 20분거리)

○ 기차

대전역(경부선, 택시이용 8천원정도, 35분거리)
서대전역(호남선, 택시이용 7천원정도, 30분거리)

UNIDO sponsored

Workshop on "Accuracy in X-ray Powder Diffraction"

- 일 시 : 2002. 11. 19 ~ 11. 21
- 장 소 : 한국표준과학연구원 기술지원동 세미나실

주최: 한국표준과학연구원
후원: UNIDO, MOST, 한국결정학회

초대의 말씀

귀하의 건승하심을 기원합니다.

저희는 XRD 분야에서 오랫동안 연구하여오신 국내외 저명 학자들과 함께 "Accuracy in X-ray Powder Diffraction"의 제목으로 워크샵을 개최하려고 합니다.

초대하오니 부디 참석하시어 유익한 정보 교류의 장(場)이 되도록 하여 주시면 감사하겠습니다.

주요내용

- Powder Pattern Indexing
- Quantitative analysis by XRD
- Rietveld Refinement

※ 참가비는 없습니다. 중식은 보조합니다.

2002년 10월

한국표준과학연구원(KRISS)

Sponsored by UNIDO, MOST, 한국결정학회

Workshop on "Accuracy in X-ray Powder Diffraction"

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