Structural and Optical Studies of Zinc Oxide Nanocrystalline Material Prepared by Green Synthesis Method

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Abstract: *In thiswork, Zincoxide(ZnO) nanoparticleswereprepared bygreen synthesis, Trachyspermumammi seeds were used as the capping agent. The formation of ZnO nano particles was confirmed by XRD studies. Also the prepared sample was subjected to FTIR studies,UV-visible spectral studies, EDAX studies and SEM studies for the characterization. The various functional groups of the sample were identified by FTIR method. The UV-visible spectral studies indicate that ZnOnano particles have thecut-off wave length at 373 nm. Theelements such as Zn and O present in the sample were found by EDAX method. The surface morphology of the synthesized ZnO nanoparticles was studied by recording the SEM images.*

Keywords:Greensynthesis, ZnO, Nanoparticle, FTIR, XRD, EDAX, SEM

1. Introduction

Nanoscience research has been rapidly increasing across the world during the last decade. It is accepted by the world scientific, industrial, government and business communities that nanoscience will be integral part in the development of future technologies. Nanotechnology will take part in an important position in the field ofenergy. Most nanoscale materials are too small to be seen with the naked eye and even with conventional laboratory microscopes. Some nanomaterials can occur naturally, such as blood borne proteinsessentialforlifeandlipidsfoundinthebloodandbody fat. Scientists, however, areparticularlyinterestedin engineered nanomaterials, whichare designed for use in many commercial materials, devices and structures. Already, thousands of common products including sunscreens, cosmetics, sportinggoods, stain-resistant clothing, tires, and electronics are manufacturedby variety of methods. Theyare also in medical diagnosis, imaging and drug delivery and in environmental remediation. The present natural energy resources will exhaust one day. The future generation willhavetolookfor thealternative energysources likesolar energyandhydrogenbasedfuels. There is considerable research is going on to tap hydrogen fuel by splitting water using sun light in presence of nanomaterials [1-3].Various types of nanoparticles such as metal oxides nanoparticles, polymer nanoparticles and metal nanoparticles have been reported [4]. Metal oxide nanoparticles such as Al_2O_3, MgO, ZrO_2, CeO_2, TiO_2, ZnO, Fe_2O_3, SnO; are the most versatile materials due their diverse properties and functionalities [5].Amongst these nanoparticles, zinc oxide (ZnO), also known as zincite has attracted much attention within the scientific community as a ‘futurematerial’ and thus an importantn-type semiconducting metal oxide [6].

Currently, investigations on the 'green' synthesis method of ZnO nanoparticles are being studied as an alternative to the chemical and physical methods which are non-compatible, toxic and costly. Unlike these methods,the 'green' synthesis method is a compatible, eco- friendlier and cheaper approach.zinc oxide (ZnO) nanoparticles are of great interest due to several favorable properties including good transparency, high electron mobility, wide band gap, and room- temperature luminescence. A wide range of nanoparticles in the form of colloids, clusters, powders, tubes, rods, wires, thin films, etc. can be prepared by a variety of methods [7].In this investigationan important nanomaterial viz. zinc oxide (ZnO) has be prepared by green synthesis and the synthesized sample was subjected to various studies.

Dhandapani etal., have prepared zincoxide nanoparticles by using Meliaazedarach leaf extract with zincnitrate as initiating material. Scanning Electron Microscopy (SEM) andTransmission Electron Microscopy (TEM) images showed hexagonal and spherical shapes of synthesized zinc oxide nanoparticles size ranges between33–36nm[8].Mirganeetal., haveprepared zinc oxide nanoparticles (ZnO NPs) by abelmoschusesculentus Linn. Various phytochemicals present leaves extract of ladys finger or the in Abelmoschus esculentus used for reduction and stabilization of agent for the synthesis of ZnONPs.Plant assisted zincoxide nanoparticles show good band gap 3.37eV and have the good photo catalytic activity in UV region [9]. Obeizietal., have used green synthesis for producing zinc oxide nanoparticles. After extraction of essential oil from leaves by hydrodistillation, it was mixed with Zinc acetate dihydrate to prepare ZnO nanoparticles and various studies have been carried out[10]. Brindhadevietal, have synthesized zinc oxide nanoparticles using biological sources like plants, fruits, bacteria, fungi, algae etc. The introduction of biological sources for the synthesis of ZnONPs will promote a safer and non-toxic approach. The biomolecules present in biological sources act as capping or coating agents to enhance the stability and potentials of the ZnONPs. The structural and chemical characterization of the synthesized ZnONPs was performed using various analytical methods [11].From the literature survey, it is observed that nobody has used *Trachyspermumammi seeds* for preparation of ZnO nanoparticles and hence *Trachyspermumammi seeds*were used to synthesizeZnO nanoparticles in this work.

2. Experimental details Materials

The materials used were Trachyspermumammi seeds, zinc acetate dihydrateand sodium hydroxide.

2.1 Preparation of plant extract

A 10 g Trachyspermumammi seed was taken and it was dried in room temperature for two days and it was ground well and washed thoroughly by demineralised water to remove the dirt and stirred it foran hour. The solution was filtered and the extract was storedand kept away from the sunlight.

2.2 Preparation of Zinc acetate dihydrate solution

Zinc acetate dihydrate (4 gm) was dissolved in 50 ml of demineralised water at a room temperature and the solution was stirred for an hour and it was kept aside for 30 min.

2.3 Synthesis of Zinc oxide nanoparticle

The prepared solution of zinc acetate dehydrate was added to the 10ml of seed extraction which was stirred well using a hot-plate magnetic stirrer for 1 hour. Then aqueous solutionof 50 ml sodium hydroxide was addeddrop wisetothe mixtureof zinc acetate dihydrate and the seed extract. Again the mixed solution was stirred for an hour. The precipitate was allowed to settle at the bottom of the

beaker [12].Then the excess water was removed by filtering the liquid and the heating process was carried out at the temperature of 110ºC for 2 hrs to evaporate the solvent and the ZnO nanoparticles were collected.

3. Results and Discussion

3.1 Powder XRD studies

X-ray diffraction (XRD) is an efficient analytical technique used to identify and characterize unknown crystalline materials. In powder XRD method, powders of a crystalline material are diffracted by X-rays. Powder X-ray diffraction is useful for confirming the identity of a solid material and determining crystallinity and phase purity.TheXRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with X- rays of a fixed wavelength and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing. The X-ray diffraction experiment requires an X-ray source, the sample under investigation and a detector topickup thediffractedX-rays. For typicalpowder patterns, data is collectedat 2θ from ~ 5° to 80° angles that are preset in the X-ray scan [13].

The prepared sample of ZnO nanoparticles has been subjected to powder X-ray diffraction(PXRD) analysis toconfirmthe latticeconstants of thesampleandtoconfirm the reflectionplanes.X-ray diffraction data gives the angle of scattering (2θ) and the corresponding intensities of diffracted beam for each reflection. The powder XRD (PXRD) pattern of ZnO nanoparticles was recorded using the powder X-ray diffractometerwith wavelength of 1.5406 Å.The recorded PXRD pattern of the sampleis shown in figure 1. The d- spacing's corresponding to different peak positions were calculated using the Bragg'slaw 2 d sin θ= n λ where d is the interplanar spacing, θ is the Bragg's angle, n is the order of diffraction and λ is the wavelength of X-rays. The Bragg's diffractionpeaks wereindexedfor thehexagonalcrystalsystem. The reflections of the powder XRD pattern of the grown crystal was indexed using the INDEXING and TREOR software packages. The broad peaks of the XRD pattern indicate that the preparedsample is a nanosample. The diffractionpeaks of sample areindexed as (100), (002), (101), (102), (110), (103) and (112), which arematched with JCPDS card No.89-1397.The sample exhibits the reflections corresponding to the hexagonal structure. The values of lattice parameters for ZnO Nanoparticles a= b=3.231Å,c=5.174Å, α=90º, β=90º and γ=120º.The obtained values of unit cell parameters are found to be well matched with the reported values [14,15].The particle size has been calculated by Debye-Scherrer's formula given by Particle size D = Kλ/β cos θ where K is a constant and it is equal to 0.9, λ is wave length of X-rays, β is full width at half maximum and θ=Bragg's angle. The obtained values of particle size of the sample are provided in the table1.The average value of particle size of ZnO nanoparticles is found to be 17.287nm.

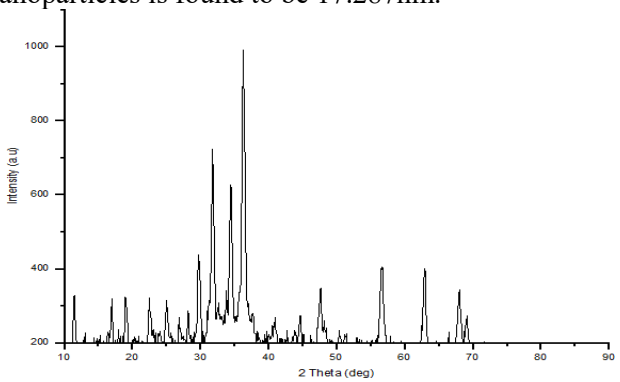

Figure.1:PowderXRDpatternofZnOnanoparticles

Table1:ValuesofTwoTheta,RelativeIntensity,hklandParticleSize of ZnO Nanoparticles

S.No.	Twotheta (degrees)	d(Å)	hkl	Particlesize (nm)
1.	31.31	2.855	100	20.132
2.	33.45	2.676	002	19.761
3.	36.77	2.443	101	14.951
4.	47.11	1.927	102	11.864
5.	56.37	1.631	110	15.546
6.	62.84	1.477	103	19.815
7.	67.92	1.378	112	18.943

3.2 FTIR Studies

Fourier Transform Infrared (FTIR) spectroscopy is a measurement technique that allows one to record infrared spectra. Nowadays, FTIR instruments are computerized which makes themfaster and more sensitive than the older dispersive instruments. It is one of the most important spectroscopic techniques used for analyzing the structural units of the unknown compounds. It also helps to identify the functional units, internal structureofthemolecules andnatureofthechemicalbondsofa compound. Absorption ofinfraredradiationsisconfinedlargelytomolecularspeciesforwhichsmallenergydifferences exist between various vibrational and rotational states. When the frequency of the incident radiation coincides with the vibrational frequency of the molecules, absorption of energy takes place. When the molecules return from the excited state to the ground state the absorbed energy is released resulting in distinct peaks in the IR spectrum. This absorption andrevealthestate of the molecules present inthesample. The KBr pellet method is more popular and has several advantages over the mull method such as low scattering loss, higher spectral resolution, the homogeneity of the sample etc. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. In this study, the KBr pellet method was used to record the IR spectra of the sample [16]. FTIR spectrum of the synthesized sample of ZnO is shown in the figure 2. Here the spectrum was recorded in the infrared region 4500–400 cm^{-1} using an FTIR spectrometer (SHIMADZU-FTIR-8400S).The spectrum reveals the presence of OH stretching and bending vibrations at 3388 cm^{-1} and 1400 cm^{-1} respectively. The plant extract contains reducing sugars which gives rise to the OH bending vibrations. The 1633 cm^{-1} peak gives thedeformationof NHb ending vibration. Theabsorption peakat 1017cm^{-1} can be assigned to the phenolic groups present in the plant extract. The effective formation of ZnO can be affirmed from the peak at 495 cm^{-1} and the Zn-OH group is due to at 778 cm^{-1}. The stretching of Zn-O is found around400–800 cm^{-1}.It is confirmed that the synthesized ZnO nanoparticles are surrounded by OH group and phenolic group and these functional groups are able to bind metalions to prevent agglomeration and thereby stabilize the medium. This suggests that the biological molecules could possibly perform dual functions of

formation and stabilization of ZnO nanoparticles [17].The FTIR spectral assignments for ZnO nanoparticles are provided in the table2.

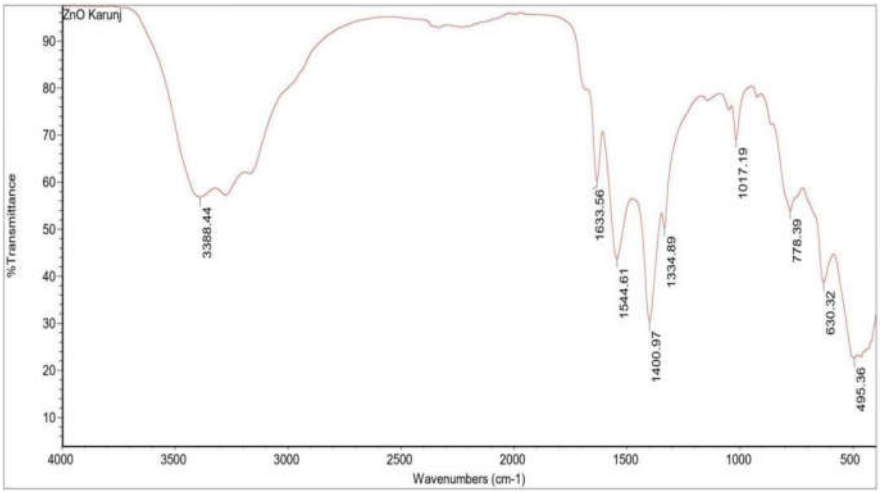

Figure. 2:FTIRspectrumofZnO nanoparticles

Table2:FTIRspectralassignments

Absorptionbands/peaks (cm^{-1})	Functionalgroups
3388	OH stretching
1633	NH bending
1544	NHdeformation
1400	OHbending
1334	C-O stretching
1017	Phenolicgroup
778	Zn-Ovibration
630	Zn-O vibration
495	Zn-OHvibration

3.3 UV Spectral Studies

Ultraviolet-visible spectroscopy deals with absorption in the UV and visible regions and the molecules undergo transitions and electrons absorb electromagnetic radiation and excited from ground state to the higher energy state. UV-visible transmittance/absorbancespectra ofthesamples arerecorded coveringthenear, visible, near-infrared region to find the transmission range to know the suitability for optical applications [18]. In this work, the UV-visible spectrum of ZnO nanoparticles was recorded on a SHIMADZU UV-240 IPC spectrophotometer in the range of 200-800 nm. The prepared sample was dispersed in ethanol and the spectrum was recorded andit is shown in the figure 3. From the results, the lower cut- off wavelength for the sample is observed to be at 373 nm and the percentage of absorption

noticed to be nearly zero. Optical band gap (E_g) was evaluated by using the relation 1240/λ where λ iscut-offwavelengthandcalculatedvalueofopticalbandgapforZnOnanoparticlesis2.69eV.

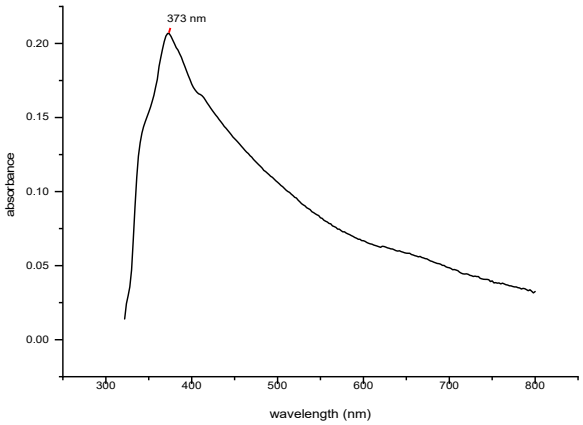

Figure No: 3 UV Tauc Plot

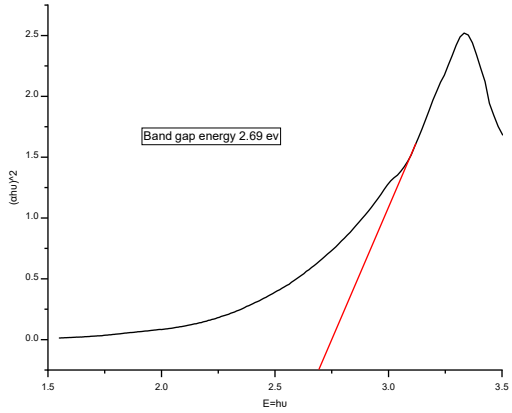

Figure No: 4 UV Tauc Plot Band Gap Energy

3.4 EDAX Spectral Studies

Energydispersivespectroscopyisananalyticaltechniqueusedfortheelemental analysisorchemicalcharacterizationofasample.ItisoneofthevariantsofX-rayfluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that eachelementh as a unique atomic structure allowing X-rays that are characteristic of an elements atomic structure to be identified uniquely from one another. The EDAX detector measures the relative bundance of emitted

X-rays versus their energy. The detector is typically lithium drifted silicon, solid state device. When an incident X-ray strikes the detector, it creates a charge pulse that is proportionalto the energy of the X-ray. The charge pulse is converted to a voltage pulse by a charge-sensitivepreamplifier. Thesignal is then sent to a multichannel analyzer wherethepulses are sorted by voltage. The energy is determined from the voltage measurement for each incident X-ray is senttoa computer for display and further data evaluation. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampledvolume.Elementswithatomicnumbersrangingfromthatofberyllium touranium can be detected. The minimum detection limits vary from approximately 0.1 to a few a to ampercent, depending on the element and the sample matrix. Quantitative results can be obtained from the relative X-ray counts at the characteristic energy levels for the sample constituents [19]. The elemental analysis was carried out for ZnO nanoparticles by employing Energy Dispersive Analysis by X-rays (EDAXor EDS) in order to confirmthe composition of elements in the sample. EDAX makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons. Fig.4 shows the EDAXspectrumof ZNO nanoparticles andthe elements suchas zinc andoxygenwere identified.

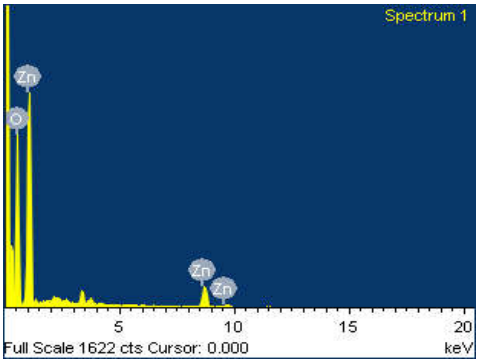

Figure.5:EDAX SpectrumofZnOnanoparticles

3.5 SEM Studies

Scanning Electron Microscope (SEM) functions exactly as their optical counterparts except that they use a focused beam of electrons instead of light to image the specimen and gain information as to its structure and composition. Electron microscopes are capable of much higher magnifications and have a greater resolving power than a light microscope, allowing it to see much smaller objects at sub cellular, molecular and atomic level. The smallest the wavelength of the illuminating sources is the best resolution of the microscope. The morphology of ZnO nanoparticles were studied using SEM and thecorresponding images areshown in thefigures 5 and 6.The figure 5 shows the morphology of the sample with magnification of x 1500 and the figure 6 shows the morphology of the sample withmagnification of x 5000. From the images, the ZnO nanoparticles are observed to be in the nanoflake like arrangement with slight agglomeration.

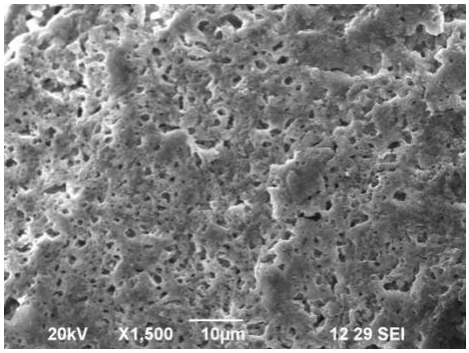

Figure No. 6: SEM Image of ZnONano Particles with magnification of x 1500

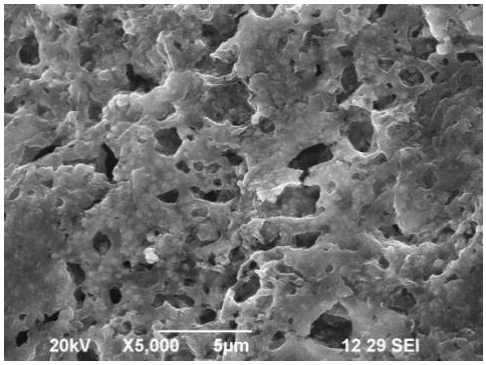

Figure No.7: SEM Image of ZnO Nano Particles with magnification of x 5000

4. Conclusion

ZnO nanoparticles have been effectively prepared by green synthesis using Nigella Sativa seeds. The synthesized sample was confirmed by powder XRD studies and it reveals thatZnO nanocrystalline sample crystallizes in hexagonal structure. Lattice parameters for ZnO nanoparticles are found to be a = b = 3.231 Å, c = 5.174 Å,$\alpha = 90^o$, $\beta = 90^o$ and $\gamma = 120^o$. By XRD studies, the average particle size of the sample was found to be 17.287 nm. FTIR spectral study indicates the presence of functional groups like OH, NH, Zn-O, phenoloicgroup etc. From UV-visible spectral method, the band gap of the sample was found to be 2.69 ev. The elements present in the ZnO nanoparticles were identified by EDAX method. The surface morphology of the sample was analyzed by SEMstudies.

5. Acknowledgement

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6. References

[1]. Drexler, K. Eric, Nanosystems: Molecular Machinery, Manufact, and Computation. New York: John Wiley & Sons (1992).
[2]. GijareMedha, Chaudhri Sharmila and Garje Anil, Int. Res. J. of Science & Engineering, pp: 29-34, (2017).
[3]. Saini Rajiv; Saini, Santosh; Sharma, Sugandha, Journal of Cutaneous and Aesthetic Surgery, 3, 32-33 (2010).
[4]. V. Mody, “Introduction to metallic nanopracticles”, Journal of Pharmacy &BioAllied Sciences, Vol. 2, No. 4, pp. 282-289, 2010
[5]. M. Fernandez-Garcia and J. Rodriguez, “Metal Oxide Nanoparticles. Manuscript submitted for publishing,” Nanomaterials: Inorganic and Bioinorganic Persepective, 2007.
[6]. V. Coleman and C. Jagadish, “Basic Properties and Applications of ZnO,” in Zinc Oxide Bulk, Thin Films and Nanostructure: Processing, Properties and Application, C. Jagadish and S. Pearton, Eds., Amsterdam, Elsevier, 2006, pp. 1-20.
[7]. S. Kulkarni, Nanotechnolology: Principles and Practices, New Delhi: Captial Publishing Company, 2015
[8]. Dhandapani KV, Anbumani D, Gandhi AD, Annamalai P, Muthuvenkatachalam BS,Kavitha P, Agricultural Biotechnology24 (2020): 101517.
[9]. Mirgane NA, Shivankar VS, Kotwal SB, Wadhawa GC, SonawaleMC,MaterialsToday: Proceedings (2020).
[10]. Z, Benbouzid H, Ouchenane S, Yılmaz D, Culha M, Bououdina M. Materials TodayCommunications.25 (2020)101553.
[11]. Brindhadevi K, Samuel MS, Verma TN, Vasantharaj S, SathiyavimalS,SaravananM, Pugazhendhi A, Agricultural Biotechnology.28 (2020)101730.
[12].Saliha B, Sipahib T, OybakDönmez, E, Journal of Ethnopharmacology. 124 (3),2009, 416–20.

[13]. H.P.Klug, L.E.Alexander, X-ray Diffraction Procedure forPolycrystallineand Amorphous materials, 2nd Edn., John Wiley and Sons,(1954).
[14]. P. Bindu, Sabu Thomas, J Theor Appl Phys (2014) 8:123–134.
[15]. Sohini Chakraborty, J. Joselin Farida, Remya Simon, S. Kasthuri, N.L. Mary Surfacesand Interfaces 19 (2020) 100488.
[16]. P.R.Griffiths and J.A.DeHoseth, Fourier Transform Infrared Spectroscopy,Wiley, Chichester (1986).
[17]. P. Manjari Mishra, S. Kumar Sahoo, G. Kumar Naik, K. Parida, Mater. Lett.160 (2015) 566–571.
[18]. A.L.Smith, Applied Infrared Spectroscopy, 2nd Edn., Holden-Day (1977).
[19].Joseph Goldstein, Scanning Electron Microscopy and X-Ray Microanalysis,Elsevier publication (2003).