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Simulated Characterization of Infrared Ceramics: Workflow Development and Experimental Comparison

by Cassidy M. Atkinson and Matthew Guziewski

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14. ABSTRACT
Characterization is a crucial step in materials development research to understand the structure and behavior of materials. This study focuses on utilizing density functional theory to develop simulated characterization methods, such as X-ray diffraction, IR spectroscopy, and Raman spectroscopy. Examples of each are given to show how these techniques may be useful to speed material processing and development.

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1. Introduction

Characterization is a crucial step in materials development research to understand the structure and behavior of materials. Historically, this has been an experimentally lead effort conducted in the laboratory using a range of techniques including X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and more. These experimental characterization methods assist in understanding material structure. However, there are limitations to experimental characterization, including equipment material cost and access. Additionally, reference databases are required for material comparison. If reference data does not exist, then it can be difficult to accurately characterize samples. To overcome these challenges, characterization methods can be simulated. Simulated characterization aids in materials processing by understanding specifically generated structures, which can then be compared to experimentally measured data.

This techinical note focuses on using simulated characterization to improve processing of materials. Density functional theory (DFT) serves as the backbone for the simulated methods. The characterization methods examined are XRD, IR spectroscopy, and Raman spectroscopy. Examples of each methodology are presented.

2. Simulated Techniques and Methodologies

This section explains the background and methodologies used to simulate XRD, IR spectroscopy, and Raman spectroscopy. An example comparing simulated and experimental data is included for each technique.

2.1 X-ray Diffraction (XRD)

XRD is a nondestructive characterization technique where an X-ray beam is directed at a sample to generate a diffraction pattern. This diffraction pattern can be used for phase identification and to determine crystal structure, lattice parameters, atomic positions, grain size, grain texture, compositional analysis, and more.[1] The premise behind XRD is when X-rays enter into the material, they can either be transmitted through or be scattered by the electrons. When X-rays are scattered, the angles between the incident radiation and the diffracted plane are both the same value, θ. For X-rays to be diffracted, a condition, known as Bragg's

law, must be met, which states that the path difference, d, between X-rays reflected from adjacent crystal planes must be an integer multiple, n, of the X-ray wavelength, λ.[2]

$$n\lambda = 2d\sin\theta \tag{1}$$

XRD spectra can be produced using only atomic positions, making it easy to simulate from a defined atomic crystal structure file. In this work, a well-defined code by Python Materials Genomics (Pymatgen)[3] was implemented. This code works by taking the input structure and calculating the reciprocal lattice. For each reciprocal point corresponding to the lattice plane, the Bragg condition is determined, and the structure factor is determined. The intensity is given by the modulus square of the structure factor, and the Lorentz polarization correction is applied. The wavelength of the radiation used can be specified to best represent experimental data, as well as the precision for structure refinement. This code also has the ability to implement Debye-Waller factors, which are temperature dependent.

The script used to simulate XRD is shown below:

```
import subprocess
from pymatgen.io.vasp import Poscar
from pymatgen.analysis.diffraction.xrd import XRDCalculator
import matplotlib.pyplot as plt

# Load POSCAR (VASP atomic position file)
file = 'POSCAR'
poscar = Poscar.from_file(file)
structure = poscar.structure

# Get XRD Pattern
XRD = XRDCalculator(wavelength='CuKa')
pattern = XRD.get_pattern(structure)

# Extract two theta and intensity
twotheta = pattern.x
intensity = pattern.y

# Plot the XRD pattern
```

```
fig, ax = plt.subplots()
markerline, stemlines, baseline = ax.stem(twotheta,
   intensity, markerfmt=' ')
plt.setp(stemlines, 'linewidth', 2)
baseline.set_xdata([0, 90])
plt.xlabel(r'2$\theta$ ($^\circ$)', size='large')
plt.ylabel('Scaled Intensities', size='large')
plt.xlim([0, 90]) # adjust to desired range
plt.xticks(size='large')
plt.yticks(size='large')
plt.tight_layout()
plt.savefig('file-name.png')
```

In summary, this script reads in a VASP atomic position file, or POSCAR (or CONTCAR) and converts the file to a structure that can be read by the pymatgen XRD Calculator module. Then, this module is used to get the XRD pattern. In this case, the wavelength of the X-ray is set to CuKa (Cu Kα), which has a wavelength of approximately 1.54 Å, and is a standard radiation used in X-ray diffraction. This value can be changed depending on the radiation of interest. The θ and intensities are extracted from the pattern, plotted using matplotlib parameters, and saved as a portable networks graphic (png).

An example of the resulting visualization can be seen in Figure 1. The material of choice is zinc sulfide (ZnS), a well-known ceramic material that has two common polymorphs: zincblende (cubic) and wurtzite (hexagonal). The simulated XRD for zincblende ZnS is compared to experimental data for ZnS produced via chemical vapor deposition. The simulated and experimental spectra show very strong agreement, although the slight peaks around 30° and 52° in the experimental data show evidence that some wurtzite phase was also present in the sample.

2.2 IR Spectroscopy

IR spectroscopy is a nondestructive characterization method that is based on the vibrations of the atoms of a molecule. In experimental practice, IR radiation is passed through a sample and a spectrum is obtained by determining what fraction of the radiation is absorbed at a particular energy.[4] The energy of the peaks in the spectrum correspond to the frequency of vibration of the molecules being examined. For IR absorptions to appear, an electric dipole moment of the molecule must

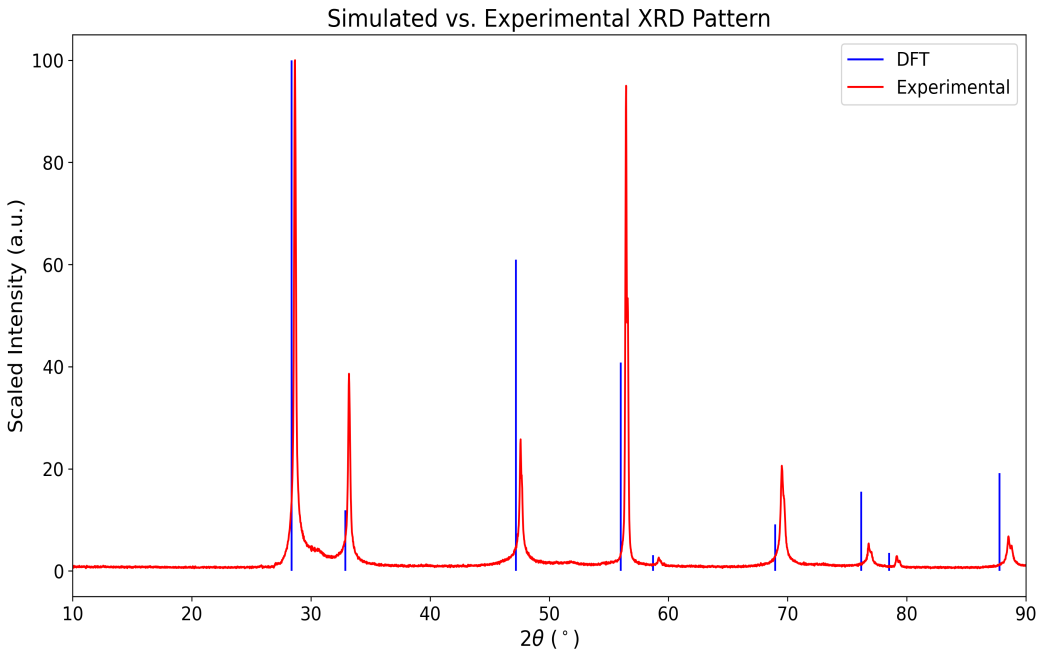

Figure 1. Simulated and experimental XRD spectra for ZnS.

change during the vibration.

IR spectroscopy can be simulated from first-principles methods. Using DFT, the harmonic approximation is the simplest place to begin. The harmonic approximation assumes that the interatomic forces can be described by a second-order Taylor expansion of the potential energy around the equilibrium positions of atoms. In this work, phonopy was used to simulate the IR spectra.[5,6] phonopy uses the finite displacement method to calculate the second-order force constants. Displacements that are large enough to produce measurable forces, but small enough to remain in the harmonic regime, are applied to individual atoms in the crystal structure. For each displaced structure, the forces on all atoms are calculated with DFT. These forces are then used to compute the second-order derivatives of the potential energy. These force constants are assembled in a matrix to construct the dynamical matrix for phonon calculations, which governs the vibrational behavior of the crystal. The eigenvalues of this matrix correspond to the phonon frequencies, and the eigenvectors describe the vibrational modes. While this method is limited to the harmonic approximation, there are ways to expand and include anharmonic lattice dynamics, or phonon-phonon interactions.

These complex dynamics can be modeled with phono3py, which focuses on three-phonon interactions.[5–7] Similar to phonopy creating displacements for the harmonic approximation, phono3py generates displacements on pairs of atoms in the structure, and then the forces are computed with DFT. Third-order force constants are calculated from these forces, which describe the interaction of three phonons. Further multi-phonon modes can be investigated with DFT through similar processes as described for the 2-phonon and 3-phonon. However, the computational cost grows siginificantly with each step. The number of phonon interaction displacement files is determined by

$$N_{displacements} = (3N)^k \tag{2}$$

where *N* is the number of atoms in the unit cell and *k* is the order of the phonon interaction, although the number of displacements may decrease depending on the symmetry of the crystal structure and the allowable distance between atoms that are examined.

The method for simulating IR spectroscopy was based on the method developed by the Skelton Group, Phonopy-Spectroscopy.[8] Phonopy-Spectroscopy calculates IR spectra by using the outputs from phonopy or phono3py calculations. The spectra are calculated based on the vibrational modes of the material, and their associated intensities are derived from the the Born effective charge tensor. IR spectra arise due to changes in the dipole moment of the material during atomic vibrations and the Born effective charge tensory describes this. Calculating the IR spectra with this method is broken down into a few steps. For second-order force constant IR spectroscopy, the steps can be broken down as follows:

1. **Relax the initial structure.**
   It is important to relax the initial structure. Phonon calculations are highly sensitive to the atomic positions and lattice parameters. If the structure is not properly relaxed, the forces acting on the atoms will not be minimized, leading to incorrect phonon frequencies. Use well-defined pseudopotentials (POTCARs), adjust the calculation parameters (INCAR), and define the Brillouin zone sampling (KPOINTS) so the structure is well converged. An example of the relaxation INCAR can be found in the Appendix.

2. **Prepare phonon frequencies and eigenvectors.**

(a) Take the relaxed structure file (CONTCAR) from the previous step and copy it into a new directory.

(b) Create finite displacement files: `phonopy -d -dim='1 1 1'`. This will generate displaced POSCAR files and `phonopy_disp.yaml`.

(c) Run single-point force calculations for each displaced structure. Each new displacement file was placed into its own directory, along with KPOINT, INCAR, and POTCAR files for a single-point force calculation. These VASP calculations were run individually. An example of the IR INCAR can be found in the Appendix.

(d) Collect forces: `phonopy -f */vasprun.xml`. The data is read from the vasprun.xml file that is output for each of the single-point force calculations and phonopy combines the calculated forces into a file called `FORCE_SETS`.

(e) Generate a `mesh.yaml` file containing the structure and gamma-point phonon frequencies and eigenvectors: `phonopy -dim='1 1 1' -fc-symmetry -mesh='1 1 1' -eigenvectors`

3. **Prepare the Born effective charge tensor.**
   Take the relaxed structure from the first step and copy it into a new directory, along with a KPOINT and POTCAR file, and an INCAR file that calculates the Born charges and dielectric tensor. Create a `BORN` file using phonopy `phonopy-vasp-born > BORN`. An example of the INCAR file needed to generate the BORN file is found in the Appendix.

4. **Generate the IR spectrum.**
   Copy `BORN` to the directory with the `phonopy_disp.yaml` and `mesh.yaml` files and run `phonopy-ir`. This will output three files: `IR-Spectrum.dat`, `IR-Spectrum.png`, and `IR-PeakTable.dat`. The linewidth, spectrum range, and other parameters can be adjusted when `phonopy-ir` is run.

For the steps above, the dimensions specified by `-dim='1 1 1'` should be adjusted to the supercell size of interest. This methodology is also compatible with phono3py for further phonon-phonon analysis; with this, it is generally

recommended to use a larger supercell for the second-order force constants compared to the third-order. Additionally, an `irreps.yaml` file that contains the irreducible representations of phonon modes grouped by Mulliken group can be generated with `phonopy -dim='1 1 1' -readfc -hdf5 -fc-symmetry -irreps='0 0 0'`, giving further information about the spectra.

An example of this methodology can be seen in Figure 2. The material of choice is silicon carbide (SiC), specifically α 6H-SiC. The experimental data for this comparison was collected using a portion of an N-doped α SiC wafer. While the primary peak is accounted for with the DFT simulated spectra, it is clear that this is not a perfect match between experimental and simulated data. There are additional phases present in the experimental data that can be associated with Si-Si interaction around 500 cm^{-1} and amorphous Si present around 860 cm^{-1}, as identified from literature.[9,10] The DFT simulated spectra solely shows the SiC peak associated with the α 6H-SiC structure because that is the crystal structure that is specifically analyzed. The deviation between the experimental and simulated data for the α 6H-SiC can be attributed to factors in the experimental sample not accounted for in the DFT simulation. Specifically, the experimental wafer is N-doped, which can cause localized strain and subtle alterations in the crystal lattice, thus affecting the material's vibrational modes, and resulting in a slight shift from the theoretical peak. This example shows that this simulated IR spectroscopy methodology is useful for gaining a deeper understanding of experimental spectra by providing a theoretical baseline of the pure material, which in turn helps to identify and assign the remaining experimental peaks to other known interactions or phases.

2.3 Raman Spectroscopy

Raman spectroscopy is similar to IR spectroscopy, but instead of examining which frequencies exhibit a vibrational mode, it examines the shift in vibration from an incident source. For a mode to be IR active, a change in dipole moment is required, while Raman modes occur from a molecule's polarizabilty. The method for simulating Raman spectroscopy was also based on the method developed by the Skelton Group, phonopy-Spectroscopy.[8] This package calculates the Raman activity tensors by taking the derivative of the high-frequency dielectric constant with respect to the normal-mode displacement. The displacements needed to

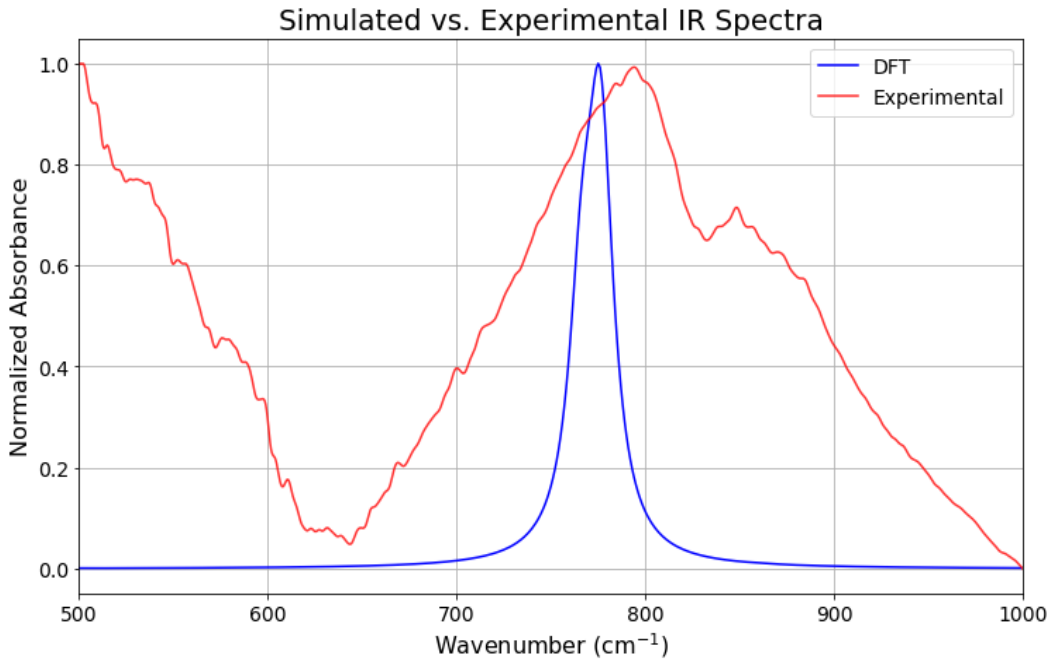

Figure 2. Simulated and experimental IR spectra for α 6H-SiC.

approximate the Raman activity are more complex than those needed for IR. For each atom in the structure, two displacement files will be generated, one with the atoms moved slightly along the mode's eigenvector and one with the atoms moved slightly against the mode's eigenvector. The postprocessing step then finds the change between the two dielectric tensors calculated, giving the Raman intensity for that single mode. This is repeated for every atom in the structure, or every mode specified based on the irreducible representations that can be found in the IR step. Additionally, the first three modes are generally acoustic modes and are skipped. For second-order force constant Raman spectroscopy, the steps can be broken down as follows:

1. **Relax the initial structure.**
   As with the IR calculation, it is important to relax the initial structure.

2. **Calculate Raman activity.**

   (a) Take the relaxed structure file (CONTCAR) from the previous step and copy it into a new directory.

(b) Generate displacement files: `phonopy-raman -d`. This will generate displaced POSCAR files and `phonopy_disp.yaml`.

(c) Run dielectric-constant calculations for each displaced structure. Each new displacement file was placed into its own directory, along with KPOINT, INCAR, and POTCAR files. These VASP calculations were run individually. An example of the INCAR file for this step can be found in the Appendix.

(d) Determine the change in dielectric tensor with respect to the atomic displacements: `phonopy-raman -r */OUTCAR`.

3. **Generate the Raman spectrum.**
   Run `phonopy-raman -p`. This will output three files: `Raman-Spectrum.dat`, `Raman-Spectrum.png`, and `Raman-PeakTable.dat`. The linewidth, spectrum range, and other parameters can be adjusted when `phonopy-raman -p` is run.

As with IR spectroscopy, this methodology is also compatible with phono3py for further phonon-phonon analysis. Additionally, the irreducible modes from the IR step can be used to determine which modes may exhibit Raman activity, which may be beneficial in decreasing the number of calculations needed for this step.

An example of this methodology can be seen in Figure 3. The material of choice is yttria (Y_2O_3). There are discrepancies between the simulated and experimental data, including a peak shift and difference in relative intensities, but the major peak regions and active Raman modes are captured by the simulated method, making it a reasonable approximation for a first-order fit. This serves as a good starting place to understand what Raman behavior should be anticipated for a material.

3. Summary

This technical note summarizes the methodology to simulate three materials characterization techniques. The simulated results show strong agreement with experimental data proving that simulated characterization from DFT can be useful as a starting point to understand a material, or to complement and gain a deeper understanding to fingerprint experimentally collected data. This methodology can help identify specific phases present, as well as serve as a theoretical baseline of

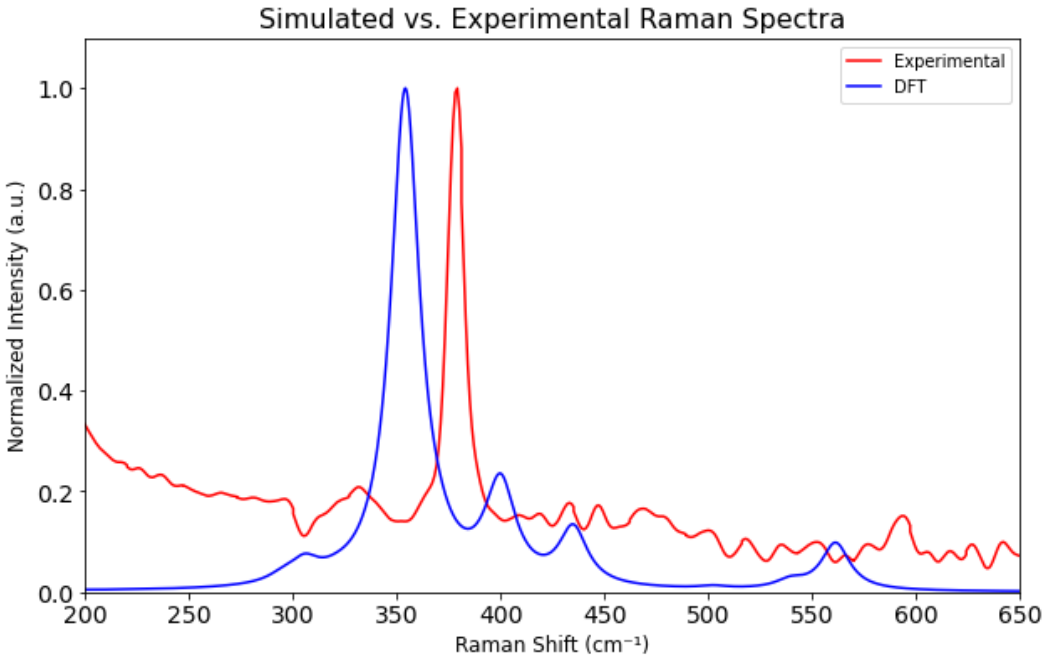

Figure 3. Simulated and experimental Raman spectra for Y_2O_3.

the pure material, to help identify and assign remaining experimental peaks to other known interactions or phases.

4. References

1. De Graef M, McHenry ME. Structure of materials: an introduction to crystallography, diffraction and symmetry. Cambridge University Press; 2012.

2. Cullity BD, Stock SR. Elements of X-ray diffraction. 3rd ed. Pearson Education; 2014.

3. Ong, SP et al. Python materials genomics (pymatgen): a robust, open-source python library for materials analysis. Computational Materials Science. 2013;68:314–319.

4. Stuart BH. Infrared spectroscopy: fundamentals and applications. John Wiley & Sons; 2004.

5. Togo A, Chaput L, Tadano T, Tanaka I. Implementation strategies in phonopy and phono3py. J Phys Condens Matter. 2023;35(35):353001.

6. Togo A. First-principles phonon calculations with phonopy and phono3py. J Phys Soc Jpn. 2023;92(1):012001.

7. Togo A, Chaput L, Tanaka I. Distributions of phonon lifetimes in Brillouin zones. Phys Rev B. 2015;91:094306.

8. Skelton, JM et al. Lattice dynamics of the tin sulphides sns 2, sns and sn 2 s 3: vibrational spectra and thermal transport. Physical Chemistry Chemical Physics. 2017;19(19):12452–12465.

9. Pitman K, Hofmeister A, Corman A, Speck A. Optical properties of silicon carbide for astrophysical applications-i. new laboratory infrared reflectance spectra and optical constants. Astronomy & Astrophysics. 2008;483(2):661–672.

10. Merazga, S et al. Deposition temperature effects on optical and structural properties of amorphous silicon carbide films. International Journal of Nanotechnology. 2013;10(5-7):587–596.

Appendix. INCAR Files

INCAR - Relaxation

```
#Global Parameters
ISTART = 1
ISPIN = 1
LREAL = .FALSE.
ENCUT = 520
LWAVE = .TRUE.
LCHARG = .TRUE.
ADDGRID = .TRUE.
LASPH = .TRUE.
PREC = Accurate
IALGO = 38
GGA = PE

#Electronic Relaxation
ISMEAR = 0
SIGMA = 0.05
NELM = 90
NELMIN = 6
EDIFF = 1E-08

#Ionic Relaxation
NSW = 100
IBRION = 2
ISIF = 3
EDIFFG = -2E-03
```

INCAR - IR

```
#Global Parameters
LREAL = .FALSE.
ENCUT = 520
LWAVE = .FALSE.
LCHARG = .FALSE.
PREC = Accurate
IALGO = 38
GGA = PE
```

```
#Electronic Relaxation
EDIFF = 1E-08
ISMEAR = 0
SIGMA = 0.01

#Ionic Relaxation
IBRION = -1
```

INCAR - BORN

```
#Global Parameters
LREAL = .FALSE.
ENCUT = 520
LWAVE = .FALSE.
LCHARG = .FALSE
ADDGRID = .TRUE.
LASPH = .TRUE.
LEPSILON = .TRUE.
PREC = Accurate
ALGO = Normal
ISYM = 0

#Electronic Relaxation
ISMEAR = 0
SIGMA = 0.05
NELM = 250
EDIFF = 1E-08

#Ionic Relaxation
NSW = 0
```

INCAR - Raman

```
#Global Parameters
LREAL = .FALSE.
ENCUT = 520
LWAVE = .FALSE
LCHARG = .FALSE
LASPH = .TRUE.
```

```
LEPSILON = .TRUE.
PREC = Accurate
ALGO = Normal
SYMPREC = 1E-06

#Electronic Relaxation
ISMEAR = 0
SIGMA = 0.01
EDIFF = 1E-07

#Ionic Relaxation
NSW = 0
ISIF =2
```

List of Symbols, Abbreviations, and Acronyms

ARL	Army Research Laboratory
DEVCOM	U.S. Army Combat Capabilities Development Command
DFT	Density Functional Theory
FTIR	Fourier Transform Infrared
IR	Infrared Spectroscopy
SiC	Silicon Carbide
XRD	X-ray Diffraction
Y_2O_3	Yttria
ZnS	Zinc Sulfide

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