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Applications of the Crystallographic Search and Analysis System CRYSTDAT in Materials Science

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Numerical database systems have recently become available online. Their enhanced search capabilities and fast retrieval of data make them a valuable tool in research. In particular, CRYSTDAT which is a search and analysis system for NBS CRYSTAL DATA has proven to be powerful in the identification of crystalline materials. In conjunction with a single-crystal x-ray diffractometer, a qualitative as well as quantitative phase determination is easily performed. The use of CRYSTDAT will be illustrated in several examples.

Key words: crystallographic database; CRYSTDAT; high T_c superconductors.

Introduction

Numerical database systems compiling inorganic crystallographic data are well established. Among the best known are the JCPDS Powder Diffraction File [1], Structure Reports (Strukturbericht) [2] and Crystal Data Determinative Tables [3]. To retrieve data from the databases in printed form, elaborate and sometimes limited and inconvenient search methods are required. In contrast, online computer systems are highly efficient. CRYSTDAT [4], which is a search and retrieval system for NBS CRYSTAL DATA [5] is accessible online and makes use of efficient search algorithms. It is therefore possible to search many parameter fields efficiently and the retrieved data can be quickly evaluated. In the following, several examples on the possible use of CRYSTDAT will be given. These examples only cover a small part of the different search routines available and use a subset of the options implemented.

Applications

Currently, NBS CRYSTAL DATA contains unit cell, composition, formula, symmetry, and reduced cell data of approximately 115,000 inorganic and organic compounds up to 1985. Using CRYSTDAT, each of these data fields can be searched individually or they can be combined through logical operators. The examples will be restricted to inorganic oxides, illustrating possible uses of CRYSTDAT in the research on high T_c ceramic superconductors. In particular, the first example will show how the database was used in the study of the Ba-Y-Cu-O system. After logging into the account and loading the database, the system replies:

ON-LINE SYSTEM

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DATABASE: CRYSTDAT

START TIME: 20:08:25

DATE: 88-06-16

The number of entries for the CRYSTDAT database=115067
The coverage is for the years 1900–1985

1. Study of the Ba-Y-Cu-O System

>find class i (*find inorganic compounds*)
--Set 1 created with 59951 hits
>set limits 1 (*limits following searches to set 1*)
--Limit Set=1
>find ele O (*find oxides*)
--Set 2 created with 31062 hits
>set limits 2
--Limit Set=2 (*limits following searches to set 2*)

a. Search for Ternary Ba-Cu-Oxides

>find ele Ba.and.Cu.and.3 (*search for ternary barium cuprates*)
--Set 3 created with 3 hits
>show 3 (*present the results of set 3*)

ID[1]: 803667 -- 1
RC: a=5.72 b=5.72 c=6.46 al=116.3 be=116.3 ga=90.0
CD: sys=tetragonal spgr(CD)=I41/amd spno=141 den=6.0(g/cc) z=4
EM: Ba Cu2 O2
FO: Ba Cu2 O2
NM: Barium dicopper(i) oxide
AC: a=5.722 c=10.064 sprg(A)=I41/amd
RF: Z. Naturforsch. B,27,296,1972

ID: 708260 -- 2
RC: a=15.81 b=15.81 c=15.81 al=109.5 be=109.5 ga=109.5
CD: sys=cubic spgr(CD)=I432 spno=211 den=7.6(g/cc) z=0
EM: Ba Cu O2
FO: Ba Cu O2
NM: Barium Copper Oxide
AC: a=18.26 spgr(A)=I432
RF: Rev. Chim. Miner.,13,440,1976

---

[1] Output abbreviations are as follows: ID=compound identification no., RC=reduced cell, CD=Crystal Data, EM=empirical formula, FO=chemical formula, NM=name, AC=author's cell, RF=journal reference.

ID : 800744 -- 3
RC : a=15.82 b=15.82 c=15.82 al=109.5 be=109.5 ga=109.5
CD : sys=cubic spgr(CD)=Im3m spno=229 den=5.6(g/cc) z=90
EM: Ba Cu O2
FO : Ba Cu O2
NM: Barium dioxocuprate
AC : a=18.27 spgr(A)=Im3m
RF : Z. Naturforsch. B,32,121,1977

b. Search for Ternary Cu-Y-Oxides

>find Y.and.Cu.and.3
--set 4 created with 2 hits
>show 4

ID : 711441 -- 1
RC : a=3.50 b=10.80 c=12.46 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic spgr(CD)=Pn21a spno=33 den=5.4(g/cc) z=4
EM: Cu2 O5 Y2
FO : Cu2 Y2 O5
NM: Copper Yttrium Oxide
AC : a=10.799 b=3.4960 c=12.456 spgr(A)=Pna21
RF : 00GRNT,,,1981

ID : 811630 -- 2
RC : a=3.52 b=3.52 c=11.42 al=90.0 be=90.0 ga=120.0
CD : sys=hexagonal spgr(CD)=P63/mmc spno=194 den=5.0(g/cc) z=2
EM: Cu O2 Y
FO : Cu Y O2
NM: Copper(i) yttrium oxide
AC : a=3.5206 c=11.418 spgr(A)=P63/mmc
RF : J. Solid State Chem.,49,232,1983

c. Search for Ternary Ba-Y-Oxides

>find ele Y.and.Ba.and.3
--Set 5 created with 4 hits
>show 5

ID : 705238 -- 1
RC : a=3.45 b=10.39 c=12.11 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic spgr(CD)=Pnab spno=60 den=7.6(g/cc) z=0
EM: Ba O4 Y2
FO : Ba Y2 O4
NM: Barium Yttrium Oxide
AC : a=10.388 b=12.110 c=3.448 spgr(A)=Pnab
RF : Mater. Res. Bull.,9,1631,1974

```
ID : N108141                                                    -- 2
RC : a=3.45 b=10.41 c=12.12 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic spgr(CD)=Pnam spno=62 den=5.8(g/cc) z=4
EM: Ba O4 Y2
FO : Ba Y2 O4
NM: Barium yttrium oxide (1˜2˜4)
AC : a=10.415 b=12.120 c=3.455 spgr(A)=Pnam
RF : Z. Naturforsch. B,19,955,1964

ID : 705239                                                     -- 3
RC : a=4.38 b=4.38 c=11.85 al=90.0 be=90.0 ga=90.0
CD : sys=tetragonal den=8.2(g/cc) z=0
EM: Ba2 O5 Y2
FO : Ba2 Y2 O5
NM: Barium Yttrium Oxide
AC : a=4.3771 c=11.852
RF : Mater. Res. Bull.,9,1631,1974

ID : 706037                                                     -- 4
RC : a=6.11 b=6.11 c=25.17 al=90.0 be=90.0 ga=120.0
CD : sys=hexagonal den=2.0(g/cc) z=0
EM: Ba3 O9 Y4
FO : Ba3 Y4 O9
NM: Barium Yttrium Oxide
AC : a=6.1102 c=25.172
RF : Mater. Res. Bull.,9,1631,1974
```

d. And Finally Search for the Quaternary Ba-Y-Cu-Oxides

```
>find ele Ba.and.Y.and Cu.and.4
  --Set 6 created with 1 hits
>show 6

ID : 809291                                                     -- 1
RC : a=5.66 b=7.13 c=12.18 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic spgr(CD)=Pbnm spno=62 den=6.2(g/cc) z=4
EM: Ba Cu O5 Y2
FO : Y2 Ba Cu O5
NM: Diyttrium barium copper oxide
AC : a=7.132 b=12.181 c=5.658 spgr(A)=Pbnm
RF : J. Solid State Chem.,43,73,1982
```

Now we can (attempt to) construct a preliminary phase diagram of the Ba-Y-Cu-O system that serves as the starting point of the analysis of this phase space.

e. Identification of a Crystalline Material

In the course of studying the phase system, small black crystals were obtained. From 6 reflections measured on the CAD4 diffractometer, a unit cell of $3.495 \times 6.23 \times 10.795$ Å was inferred. This unit cell serves as the starting point for a database search to identify the phase. In this case, the reduced cell is searched with a preset tolerance to retrieve all phases with similar lattice parameters.

>cells (*calculate the reduced cell and set up the search parameters*)
---Input Cell---
a ? > 3.495
b ? > 6.23 (*if blank, default is the previous value*)
c ? > 10.795
alpha ? > (*the default is 90 °*)
beta ? > (*if blank, default is the previous value*)
gamma ? >
Lattice Type ? (*default P*) >
Tolerance ? (*default 0.10*) >

>Input cell+vol.	3.50	6.23	10.80	90.00	90.00	90.00	235.05
>Lattice type	P						
>Red. Cell+Vol	3.49	6.23	10.79	90.00	90.00	90.00	235.05
>Niggli Matrix	12.215	38.813	116.532				
	0.000	0.000	0.000				
>Metric Symmetry	Orthorhombic						
>Tolerance for cell match	0.100						

Search the data base? (yes/no)>y
--Set 7 created with 0 hits

The database was searched with the reduced cell of the lattice with edges of 3.49, 6.23, and 10.795 Å. No matches were found. However, the unit cell determined may be too small (a subcell) because some reflections could have been missed on the diffractometer. The database is searched again, but this time, possible supercells are included in the search.

>cells
---Input Cell---
a ? > 3.495
b ? > 6.23
c ? > 10.795
alpha ? >
beta ? >
gamma ? >
Lattice Type ? (*default P*) >
Tolerance ? (*default 0.10*) >

>Input cell+vol.	3.50	6.23	10.80	90.00	90.00	90.00	235.05
>Lattice type	P						
>Red. Cell+Vol.	3.49	6.23	10.79	90.00	90.00	90.00	235.05
>Niggli Matrix	12.215	38.813	116.532				
	0.000	0.000	0.000				
>Metric Symmetry	Orthorhombic						
>Tolerance for cell match	0.100						

Search the data base? (yes/no)>n

The database is not searched with the original cell. Instead, a supercell search [6] *will be carried out. CRYSTDAT is instructed to generate possible supercells of 2× the volume of the input cell. After the supercells have been generated, the database is searched.*

Sub-/Super- cells calculated? (YES/NO)
where sub-cell (input cell vol.) / multiplicity
and super-cell (input cell vol.) * multiplicity>y
Sub-cell ? (yes/no)>n
Super-cell ? (yes/no)>y
Multiplicity ? (*2/3/4/5/6/7 ... etc*)>2

Super-cells of 2 times the volume of the input cell

a	b	c	al	be	ga	vol
3.495	6.230	21.590	90.0	90.0	90.0	470
3.495	12.460	12.464	120.0	90.0	90.0	470
6.230	6.990	11.347	107.9	90.0	90.0	470
6.990	7.143	11.347	81.3	72.1	60.7	470
3.495	10.795	12.460	90.0	90.0	90.0	470
6.990	7.143	10.795	90.0	90.0	119.3	470
6.230	6.990	10.795	90.0	90.0	90.0	470

Search the data base? (yes/no)>y

NOW SEARCHING

The database is now searched including all the above given supercells of multiplicity 2.

--Set 8 created with 31 hits

In this set of retrieved entries, we find the following one:

ID : 711441 -- 1
RC : a=3.50 b=10.80 c=12.46 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic spgr(CD)=Pn21a spno=33 den=5.4(g/cc) z=4
EM: Cu2 O5 Y2
FO : Cu2 Y2 O5
NM: Copper Yttrium Oxide
AC : a=10.799 b=3.4960 c=12.456 spgr(A)=Pna21
RF : 00GRNT,,,1981

Supercell 5 from the above list of supercells matched a cell in the database of a compound with the expected elemental composition. In this way, both the correct lattice and an accurate composition of the small black crystals were determined in roughly 30 minutes.

2. Study of the Bi-Sr-Ca-Cu-O System

In the case of the Bi-Sr-Ca-Cu-O superconductors, the analogous searches are easily done.

a. Search for Ternary Bi-Cu Oxides

>find ele Bi.and.Cu.and.3
--Set 9 created with 4 hits
>show 9

ID : B034138 -- 1
RC : a=5.80 b=8.48 c=8.48 al=90.0 be=90.0 ga=90.0
CD : sys=tetragonal spgr(CD)=P4/ncc spno=130 den=8.0(g/cc) z=2
EM: Bi4 Cu O7
FO : Bi4 Cu O7
NM: Bismuth copper oxide (4~1~7)
AC : a=8.481 c=5.803 spgr(A)=P4/ncc
RF : An. Acad. Brasil. Cienc.,38,35,1966

ID : 804574 -- 2
RC : a=5.81 b=6.67 c=6.67 al=79.0 be=64.1 ga=64.1
CD : sys=tetragonal spgr(CD)=I4 spno=79 den=8.6(g/cc) z=4
EM: Bi2 Cu O4
FO : Cu Bi2 O4
NM: Copper dibismuthate(iii)
AC : a=8.484 c=5.813 spgr(A)=I4
RF : Z. Anorg. Allg. Chem.,426,1,1976

ID : 704311 -- 3
RC : a=5.81 b=8.51 c=8.51 al=90.0 be=90.0 ga=90.0
CD : sys=tetragonal spgr(CD)=P4/ncc spno=130 den=8.6(g/cc) z=4
EM: Bi2 Cu O4
FO : Cu Bi2 O4
NM: Copper Bismuth Oxide
AC : a=8.510 c=5.814 spgr(A)=P4/ncc
RF : C. R. Hebd. Seances Acad. Sci. Ser. C,276,1105,1973

ID : 810281 -- 4
RC : a=5.81 b=8.51 c=8.51 al=90.0 be=90.0 ga=90.0
CD : sys=tetragonal spgr(CD)=P4/ncc spno=130 den=8.6(g/cc) z=4
EM: Bi2 Cu O4
FO : Cu Bi2 O4
NM: Bismuth copper oxide
AC : a=8.510 c=5.814 spgr(A)=P4/ncc
RF : Bull. Soc. Fr. Mineral. Cristallogr.,99,193,1976

b. Search for Ternary Bi-Sr-Oxides

>find ele Bi.and.Sr.and.3
--Set 10 created with 4 hits
>show 10

ID : B028466 -- 1
RC : a=3.95 b=3.95 c=9.64 al=78.2 be=78.2 ga=60.0
CD : sys=rhombohedral den=6.0(g/cc) z=0
EM: Bi38 O59 Sr2
FO : Bi38 Sr2 O59
NM: Bismuth strontium oxide (38~2~59)
AC : a=3.952 c=28.09 spgr(A)=R
RF : J. Res. Nat. Bur. Stand. Sect. A,68,197,1964

ID : 805401 -- 2
RC : a=3.97 b=3.97 c=9.75 al=78.2 be=78.2 ga=60.0
CD : sys=rhombohedral spgr(CD)=R-3m spno=166 den=7.8(g/cc) z=9
EM : Bi0.76 O1.38 Sr0.23
FO : Bi0.765 Sr0.235 O1.383
NM : Bismuth strontium oxide (.8/.2/1.1)
AC : a=9.75 al=23.49 spgr(A)=R-3m
RF : J. Solid State Chem.,35,192,1980

ID : 812013 -- 3
RC : a=3.97 b=3.97 c=9.74 al=78.2 be=78.2 ga=60.0
CD : sys=rhombohedral spgr(CD)=R-3m spno=166 den=7.8(g/cc) z=4
EM : Bi1.72 O3 Sr0.53
FO : Bi1.72 Sr0.53 O3
NM : Bismuth(iii) strontium(13/4) oxide
AC : a=3.971 c=28.41 spgr(A)=R-3m
RF : Solid State Ionics,3,457,1981

ID : 709884 -- 4
RC : a=4.26 b=9.60 c=9.60 al=87.2 be=77.2 ga=77.2
CD : sys=tetragonal spgr(CD)=I4/m spno=87 den=7.2(g/cc) z=0
EM : Bi1.10 O2.55 Sr0.90
FO : Sr0.9 Bi1.1 O2.55
NM : Strontium Bismuth Oxide
AC : a=13.239 c=4.257 spgr(A)=I4/m
RF : Rev. Chim. Miner.,15,153,1978

c. Search for Bi-Cu-Sr or Bi-Cu-Ca Compounds with 4 or 5 Elements

>find ele Bi.and.Cu.and.Sr.and.5
--Set 11 created with 0 hits
>find ele Bi.and.Cu.and.Sr.and.4
--Set 12 created with 0 hits
>find ele Bi.and.Ca.and.Cu.and.4
--Set 13 created with 0 hits
>find ele Bi.and.Cu.and.Ca.and.5
--Set 14 created with 0 hits

No entries containing 4 and 5 elements were found.

d. Find materials with lattices related to that of a superconducting crystal

From the x-ray study of a superconducting crystal, we obtained a cell of approximately 5.44 × 5.43 × 30.8 Å. This cell data can be used to retrieve compounds that may be structurally related to the superconductors. For this purpose, tetragonal or orthorhombic cells are retrieved and searched for their c-axis values given by the authors.

Carry out several searches to generate SET 17 containing inorganic materials with Bi and O; restrict next search to this set.

>Find sys O.or.T (*orthorhombic or tetragonal systems only*)
--Set 18 created with 244 hits
>Set limits 18 (*limits now set to inorganic bismuth oxides belonging to the orthorhombic or tetragonal systems.*)

--Limit Set=18

>find cc 28.to.34 (*find compounds with the author's c-axis between 28 and 34* Å)

--Set 19 created with 8 hits

In this way, compounds with unit cell c-axes between 28 to 34 Å *are retrieved more efficiently than by using the "cells" command.*

>show 19

ID : 711644 -- 1
RC : a=3.83 b=3.83 c=33.62 al=90.0 be=90.0 ga=90.0
CD : sys=tetragonal den=7.4(g/cc) z=0
EM: Bi3 F O11 Pb Ti3
FO : Pb Bi3 Ti3 O11 F
NM: Lead Bismuth Titanium Oxide Fluoride
AC : a=3.833 c=33.62 spgr(A)=P4/mm
RF : J. Solid State Chem.,36,349,1981

ID : B019359 -- 2
RC : a=3.84 b=3.84 c=16.64 al=96.6 be=96.6 ga=90.0
CD : sys=tetragonal spgr(CD)=I4/mmm spno=139 den=8.0(g/cc) z=2
EM: Bi4 O12 Ti3
FO : Bi4 Ti3 O12
NM: Bismuth titanium oxide (4^3^12)
AC : a=3.841 c=32.83 spgr(A)=I4/mmm
RF : Ark. Kemi,1,499,1949

ID : B024961 -- 3
RC : a=3.92 b=3.92 c=14.71 al=97.7 be=97.7 ga=90.0
CD : sys=tetragonal den=7.2(g/cc) z=2
EM: Bi3 Br3 Ca O4
FO : Bi3 Ca Br3 O4
NM: Bismuth calcium bromide oxide (3^1^3^4)
AC : a=3.92 c=28.90 spgr(A)=I
RF : Z. Anorg. Allg. Chem.,248,121,1941

ID : B024960 -- 4
RC : a=3.98 b=3.98 c=14.66 al=97.8 be=97.8 ga=90.0
CD : sys=tetragonal spgr(CD)=I4/mmm spno=139 den=7.4(g/cc) z=2
EM: Bi3 Br3 O4 Sr
FO : Bi3 Sr Br3 O4
NM: Bismuth strontium bromide oxide (3^1^3^4)
AC : a=3.976 c=28.78 spgr(A)=I4/mmm
RF : Z. Anorg. Allg. Chem.,246,115,1941

ID : B024962 -- 5
RC : a=4.04 b=4.04 c=16.23 al=97.2 be=97.2 ga=90.0
CD : sys=tetragonal spgr(CD)=I4/mmm spno=139 den=7.4(g/cc) z=2
EM: Bi3 I3 O4 Sr
FO : Bi3 Sr I3 O4
NM: Bismuth strontium iodide oxide (3^1^3^4)
AC : a=4.043 c=31.95 spgr(A)=I4/mmm
RF : Z. Anorg. Allg. Chem.,250,173,1942

ID : 709204 -- 6
RC : a=5.40 b=5.44 c=29.05 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic den=3.0(g/cc) z=0
EM: Bi7 Nb O21 Ti4
FO : Bi7 Ti4 Nb O21
NM: Bismuth Titanium Niobium Oxide
AC : a=5.44 b=5.40 c=29.05 spgr(A)=P63
RF : J. Less-Common Metals,48,319,1976

ID : 805515 -- 7
RC : a=5.41 b=5.45 c=16.64 al=99.4 be=90.0 ga=90.0
CD : sys=orthorhombic spgr(CD)=C2ca spno=41 den=8.0(g/cc) z=4
EM: Bi4 O12 Ti3
FO : Bi4 Ti3 O12
NM: Tetrabismuth trititanium oxide
AC : a=5.448 b=5.411 c=32.83 spgr(A)=B2cb
RF : Ferroelectrics,3,17,1971

ID : N110983 -- 8
RC : a=5.41 b=5.45 c=32.82 al=90.0 be=90.0 ga=90.0
CD : sys=orthorhombic den=8.0(g/cc) z=4
EM: Bi4 O12 Ti3
FO : Bi4 Ti3 O12
NM: Bismuth titanium oxide (4~3~12)
AC : a=5.411 b=5.449 c=32.82
RF : J. Electrochem. Soc.,116,832,1969

As it turns out, the last entry served as a starting point for the successful refinement of the Bi-Sr-Ca-Cu-O superconductor phase.

The set of commands a user has to remember is small and the commands themselves are self explanatory making CRYSTDAT an efficient tool in materials research.

References

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