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NATIONAL BUREAU OF STANDARDS REPORT

10512

THE CALCIUM SULFATE–WATER SYSTEM

2. INFRARED SPECTROSCOPIC, X–RAY POWDER DIFFRACTION AND SCANNING ELECTRON MICROSCOPIC STUDIES

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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2. INFRARED SPECTROSCOPIC, X–RAY POWDER DIFFRACTION AND SCANNING ELECTRON MICROSCOPIC STUDIES

by

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PREFACE

A thorough investigation of the properties of gypsum has been undertaken with the expectations that such studies will give pertinent information to the behavior of gypsum in cement and as a plaster. Initial research will concentrate on the basic properties of gypsum ($CaSO_4 \cdot 2H_2O$) and the hemihydrate ($CaSO_4 \cdot 1/2H_2O$). Later research will be devoted to behavior of gypsum plaster and of the use of gypsum as a set retarder in cement.

ABSTRACT

This is the second in a series of reports on the $CaSO_4$-H_2O system.

Infrared spectroscopy, scanning electron microscopy and x-ray powder diffraction analysis were used to ascertain if any structural differences could be found between α- and β-$CaSO_4 \cdot 1/2H_2O$. Their x-ray powder diffraction patterns were slightly different with 2θ in the range of 48 to 50°. Crystals of $CaSO_4 \cdot 2H_2O$ and β-$CaSO_4 \cdot 1/2H_2O$ were found by scanning electron microscopy to have plately forms while crystals of α-$CaSO_4 \cdot 1/2H_2O$ were rod-shaped with hexagonal faces. The infrared spectrum of α-$CaSO_4 \cdot 1/2H_2O$ was the same as the spectrum of the β form.

1. INTRODUCTION

The crystal structure of $CaSO_4 \cdot 2H_2O$ has been elucidated by x-ray diffraction measurements [1] 1/, infrared spectroscopy [2], and neutron diffraction studies [3]. The lower hydrated member of the series, $CaSO_4 \cdot 1/2H_2O$, has not been so thoroughly investigated and whether structural difference exist between the α- and β- forms of $CaSO_4 \cdot 1/2H_2O$ has not been unequivocally resolved. The present study was undertaken with the hope of ascertaining if α- and β-$CaSO_4 \cdot 1/2H_2O$ have dissimilar structures.

1/ Numbers in brackets refer to literature references at the end of this report.

The x-ray powder diffraction patterns of α- and β-$CaSO_4 \cdot 1/2H_2O$ have been reported [4] to slightly differ with 2θ in the range of 48 to 50° and this difference was investigated in the present study. Included in this report, also, are the results of infrared spectroscopic and scanning electron microscopic studies on α- and β-$CaSO_4 \cdot 1/2H_2O$. Similar studies were carried out on $CaSO_4 \cdot 2H_2O$ for comparative purposes.

2. EXPERIMENTAL

2.1 Materials

The materials, $CaSO_4 \cdot 2H_2O$, α- and β-$CaSO_4 \cdot 1/2H_2O$, used in this study have been described in Part 1 of this series.

2.2 Infrared Spectra

The infrared transmission spectra of $CaSO_4 \cdot 2H_2O$ and α- and β- $CaSO_4 \cdot 1/2H_2O$, between 580 to 4,000 cm^{-1}, were recorded using a Perkin-Elmer Model 421 Double Beam Spectrophotometer.

Specimens were prepared for infrared studies by either the nujol mull or the KBr pellet technique. The KBr pellets were made by thoroughly mixing 1 to 2 mg of sample with 400-450 mg of Harshaw optical grade KBr and then pressing the powder to 18,000 psi under vacuo. Bank nujol mulls or KBr pellets were used as references in the double beam spectrophotometer.

2.3 Scanning Electron Microscopy

Scanning electron microscope photographs of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ were taken using a Cambridge Stereo Scan Scanning Electron Microscope. The specimens were coated with a thin deposit of carbon to reduce charge build-up. Magnification ratios were between 900 and 1000.

2.4 X-ray Powder Diffraction Patterns

The X-ray Powder Diffraction Patterns were obtained by Mr Harold Swanson, Institute for Materials Research, National Bureau of Standards, using unfiltered Cu Kα radiation.

3. RESULTS

3.1 Infrared Spectra

The infrared spectra of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ dispersed in KBr pellets, are reproduced in Figure 1. Observed frequencies and assignments of the absorption bands of $CaSO_4 \cdot 2H_2O$ are listed in Table 1 and the corresponding data are given in Table 2 for α- and β-$CaSO_4 \cdot 1/2H_2O$. The present assignments are based upon those given by Hass and Sutherland [2] for single crystals of $CaSO_4 \cdot 2H_2O$.

The absorption bands of specimens prepared by the nujol mull method were broad and badly resolved (Figure 2). However, their positions agreed reasonably well with the analogous bands observed with KBr pellets. This positional correlation, incidently, is the basis for assuming that no serious structural or compositional modifications were induced in the samples by the KBr pellet technique.

The infrared spectrum of $CaSO_4 \cdot 2H_2O$ in a KBr pellet, heated at 109°C in an air oven for 16 hours is shown in Figure 3. The ν_1 (H_2O) fundamentals of both $CaSO_4 \cdot 2H_2O$ and β-$CaSO_4 \cdot 1/2H_2O$ and the ν_3 (H_2O) fundamental of β-$CaSO_4 \cdot 1/2H_2O$ are clearly present. Infrared spectroscopy, therefore, can be used to follow dehydration and rehydration processes within the $CaSO_4$-H_2O system.

3.2 Scanning Electron Micrograms

The scanning electron microscope photographs of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ are shown in Figures 4, 5 and 6, respectively. While crystals of both $CaSO_4 \cdot 2H_2O$ and β-$CaSO_4 \cdot 1/2H_2O$ have plately shapes, those of α-$CaSO_4 \cdot 1/2H_2O$ have a more flakely surface compared to $CaSO_4 \cdot 2H_2O$. In contrast to β-$CaSO_4 \cdot 1/2H_2O$, the crystals of α-$CaSO_4 \cdot 1/2H_2O$ are rod-shaped with hexagonal faces.

3.3 X-ray Powder Diffraction Patterns

The x-ray powder diffraction patterns of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ are reproduced in Figures 7, 8 and 9, respectively. These patterns are in agreement with those previously reported.

The only difference observed between the patterns of α- and β-$CaSO_4 \cdot 1/2H_2O$ was in a peak located between 48 and 50°, which is shown with an expanded scale in Figure 10. The peak of α-$CaSO_4 \cdot 1/2H_2O$ had triplet structure while no well resolved structure was observed in the peak of β-$CaSO_4 \cdot 1/2H_2O$.

4. DISCUSSION

4.1 Infrared Spectra

The infrared absorption spectra of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ dispersed in KBr pellets (Figure 1) were much better resolved than the corresponding nujol mull spectra (Figure 2) and only the former spectra will be discussed. It is instructive to first analyze the spectrum of $CaSO_4 \cdot 2H_2O$ and then to compare the spectra of α- and β-$CaSO_4 \cdot 1/2H_2O$.

The infrared absorption spectrum of $CaSO_4 \cdot 2H_2O$ in KBr pellets was generally similar to the spectrum of single crystals of gypsum, which has been studied by Hass and Sutherland [2]. The following analysis of the spectrum is based upon the site symmetry concept [5]. First the vibration modes attributed to the SO_4^{2-} ions are considered followed by a discussion of the H_2O vibrations. The free SO_4^{2-} ion has tetrahedral symmetry, T_d, and has four vibrational modes, ν_1 (A_1), ν_2 (E) and ν_3 (T_2) and ν_4 (T_2), with only the latter two modes having ungerade symmetry, $_u$, and thus being infrared active. The $CaSO_4 \cdot 2H_2O$ crystal has C_{2h} symmetry [1], with the C_2 crystal axis coinciding with a C_2 axis of each SO_4^{2-} group. The crystalline field of $CaSO_4 \cdot 2H_2O$ is weaker than the intramolecular forces within the SO_4^{2-} ion and this results in a small perturbation of the internal vibrations of the SO_4^{2-}. While this small perturbation does cause a lifting of all vibrational degenerary because of a reduction in the effective symmetry from T_d to the site symmetry of C_{2h}, only small energy splittings in the free SO_4^{2-} vibrational frequencies takes place. The number of infrared active modes is increased from two to nine, as seen in the correlation chart of Table 3, and six of these fundamentals were observed in the present study (Table 1). Two fundamentals arising from the ν_2 mode of T_d symmetry are expected to have frequencies in the 400-500 cm^{-1} range, which is beyond the capacity of the spectrophotometer used in this work. The other missing fundamental, bu (ν_3), should lie between bu (ν_3), 1106 cm^{-1}, and a_μ (ν_3), 1133 cm^{-1}, but apparently was obscured by these absorptions. Measured vibrational splittings were small with the maximum splitting of ν_4 being 68 cm^{-1} and a splitting of 27 cm^{-1} was found in ν_3.

The interpretation of the H_2O fundamentals in $CaSO_4 \cdot 2H_2O$ is based upon the coupling of phonons with the molecular vibrations of H_2O [3,6]. Isolated H_2O molecules belong to the C_{2v} point group and have three fundamental modes ν_1, ν_2 and ν_3 that are all infrared active. Each unit cell of $CaSO_4 \cdot 2H_2O$ has four H_2O molecules [1] and the crystal internal modes can be constructed by the superposition of the molecular modes of H_2O in the unit cell, in such a manner that the crystal internal modes are representations of C_{2h}. When the H_2O molecules are not interacting with each other each molecular mode becomes fourfold degenerate in the crystal. A small amount of coupling, however, leads to a lifting of the degenerary and each molecular fundamental splits into four crystal modes belonging to symmetry species of the C_{2h}

point group, as shown in Table 4. Two of the four crystal modes arising from each molecular mode belong to the ungerade type, μ, and therefore are infrared active. Since the coupling forces are smaller than the intramolecular forces within the H_2O molecule the splittings in the ν_1, ν_2 and ν_3 frequencies should be small.

The lifting of degenerary as given in Table 4 was observed in the infrared spectrum of single crystals of gypsum, with the frequency splittings being 62, 20 and 47 cm^{-1}, respectively, in ν_2, ν_1, and ν_3 [2]. In the present study of $CaSO_4 \cdot 2H_2O$ in KBr pellets only the splitting in ν_2 was observed and the value was 60 cm^{-1}. The only previously unreported absorption band observed in the present study was that at 3240 cm^{-1} which is attributed to the first overtone of bu(ν_2).

It was impossible to distinguish between the two forms of $CaSO_4 \cdot 1/2H_2O$ on the basis of their infrared adsorption spectra (Figure 1 and Table 2). Several interesting differences, however, were noted between the spectra of the α- and β-$CaSO_4 \cdot 1/2H_2O$ set and the spectrum of $CaSO_4 \cdot 2H_2O$. The portions of the spectra lying below 1600 cm^{-1}, attributed to the SO_4^{2-} group, were the same in both cases except for some slight frequency shifts. The main differences were associated with the H_2O frequencies and the following is a discussion of the pertinent observations.

No splittings in ν_1, ν_2 or ν_3 of H_2O were found in the spectra of the $CaSO_4 \cdot 1/2H_2O$ set. This is reasonable for the removal of 3/2 molecules of H_2O from $CaSO_4 \cdot 2H_2O$ changes the unit cell and should decouple the interactions between the H_2O molecules thereby preventing the type of photon-vibrational coupling active in $CaSO_4 \cdot 2H_2O$.

Values of ν_1, ν_2 and ν_3 of H_2O for $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ are compared in Table 5. Included, also, are values for nonhydrogen bonded H_2O, in the gaseous state [7], and for strongly hydrogen bonded liquid H_2O [8]. The increases of 139 and 89 cm^{-1} in ν_1 and ν_3, respectively, in going from $CaSO_4 \cdot 2H_2O$ to the $CaSO_4 \cdot 1/2H_2O$ set is an interesting phenomenon. In $CaSO_4 \cdot 2H_2O$ and presumably in both α- and β-$CaSO_4 \cdot 1/2H_2O$ the hydrogen bonding is between H_2O and the SO_4^{-2} ion rather than between H_2O molecules. Usually a decrease in the number of H_2O molecules in a system where the hydrogen bonding is between H_2O and the anion results in a slight decrease in the values of ν_1 and ν_3, indicative of the formation of stronger hydrogen bonds. Furthermore, lattice H_2O normally absorbs at 3200-3550 cm^{-1} (ν_1 and ν_3) and at 1600-1630 cm^{-1} (ν_2) [9,10]. While the absorptions for $CaSO_4 \cdot 2H_2O$ are within these regions, the ν_1 and ν_3 frequencies for the $CaSO_4 \cdot 1/2H_2O$ set are substantially higher than those associated with lattice H_2O. These observations do suggest a weaker hydrogen bonding system in α- and β-$CaSO_4 \cdot 1/2H_2O$ than in $CaSO_4 \cdot 2H_2O$. The H_2O molecules are possibly only interstitially held in the crystal lattices of α- and β-$CaSO_4 \cdot 1/2H_2O$.

4.2 Scanning Electron Micrograms

The scanning electron microgram of $CaSO_4 \cdot 2H_2O$ (Figure 4) shows that the crystals have plately shapes. This is consistent with the structural determinations by Wooster [1] showing that gypsum has a layer lattice and layers are held together by hydrogen bonding between H_2O molecules and SO_4^{2-} ions. Reducing the extent of interlayer hydrogen bonding should weaken the cohension between layers, which possibly lead to the flaking characteristics of the crystals of β-$CaSO_4 \cdot 1/2H_2O$ (Figure 5). Since both $CaSO_4 \cdot 2H_2O$ and β-$CaSO_4 \cdot 1/2H_2O$ have plately shapes, it seems that the integrity of the layer lattice was not strongly, if at all, perturbed by the partial dehydration of $CaSO_4 \cdot 2H_2O$.

The shape of crystals of α-$CaSO_4 \cdot 1/2H_2O$ was observed to be rod-like with hexagenal faces (Figure 6). This suggests either a tri-dimensional lattice for α-$CaSO_4 \cdot 1/2H_2O$, in contrast with the two-dimensional lattice of β-$CaSO_4 \cdot 1/2H_2O$, or the intertwining of smaller crystals within large crystals of α-$CaSO_4 \cdot 1/2H_2O$.

4.3 X-ray Analysis

Difference in the x-ray powder diffractions patterans of α- and β-$CaSO_4 \cdot 1/2H_2O$ only will be discussed, since the crystal structure of $CaSO_4 \cdot 2H_2O$ has been determined [1] and the differences in the patterns of $CaSO_4 \cdot 2H_2O$ and the $CaSO_4 \cdot 1/2H_2O$ set have been previously explored [11,12].

The x-ray powder diffraction patterns of α- and β-$CaSO_4 \cdot 1/2H_2O$, with 2θ in the range of 10 to 70°, are reproduced in Figures 8 and 9, respectively. No differences were observed at this scale. In a slower scan, with an enlarged scale, however, a slight difference was observed in a peak located between 48 and 50° (Figure 10). The peak of α-$CaSO_4 \cdot 1/2H_2O$ has triplet character while that of β-$CaSO_4 \cdot 1/2H_2O$ has a single shoulder. This difference has been attributed to stacking fault crystal imperfections by R. J. Morris [4] and to the intergrowth of a sub-structure of lower symmetry by Gay [13]. The crystal structures of α- and β-$CaSO_4 \cdot 1/2H_2O$, however, have not been unequivocally determined, despite considerable work [14,15]. Therefore, no definite conclusions from the pattern differences between α- and β-$CaSO_4 \cdot 1/2H_2O$ can presently be given.

5. SUMMARY

The possibility of structural differences existing between α- and β-$CaSO_4 \cdot 1/2H_2O$ was investigated by infrared spectroscopy, scanning electron microscopy, and x-ray powder diffraction analysis. Similar studies were carried out on $CaSO_4 \cdot 2H_2O$ for comparative purposes.

The infrared spectrum of α-$CaSO_4 \cdot 1/2H_2O$, studied from 580 to 4000 cm^{-1}, was the same as that of the β-form. The essential difference between these spectra and the spectrum of $CaSO_4 \cdot 2H_2O$ concerned the number and frequencies of the H_2O vibrations. Because of the high frequencies of $\nu_1(H_2O)$, 3528 cm^{-1}, and

$\nu_3(H_2O)$, 3604 cm^{-1}, for the $CaSO_4 \cdot 1/2H_2O$ pair, it is suggested that the H_2O molecules are only interstitially held in $CaSO_4 \cdot 1/2H_2O$.

Scanning electron micrograms show that crystals of $CaSO_4 \cdot 2H_2O$ and β-$CaSO_4 \cdot 1/2H_2O$ have plately forms while crystals of α-$CaSO_4 \cdot 1/2H_2O$ are rod-shaped with hexagonal faces. A slight difference was observed between the x-ray powder diffraction patterns of α- and β-$CaSO_4 \cdot 1/2H_2O$ with 2θ in the region of 48 to 50°.

The results of infrared, scanning electron microscope and x-ray powder diffraction studies indicate that structural differences between α- and β-$CaSO_4 \cdot 1/2H_2O$ are small. However, x-ray diffraction and neutron diffraction studies on good single crystals are necessary before definitive structural determinations can be made.

6. ACKNOWLEDGMENTS

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Table 1. Observed Frequencies and Assignments of Infrared Absorption Bands of $CaSO_4 \cdot 2H_2O$

Frequency (cm^{-1})	Assignment	Symmetry Species
595	$\nu_4(SO_4)$	a_u
626	$\nu_4(SO_4)$	b_u
660 sh [a]	unassigned	-
663	$\nu_4(SO_4)$	b_u
996	$\nu_1(SO_4)$	a_u
1106	$\nu_3(SO_4)$	b_u
1133	$\nu_3(SO_4)$	a_u
1612	$\nu_2(H_2O)$	b_u
1672	$\nu_2(H_2O)$	a_u
2110	$\nu_3+\nu_1(SO_4)$	b_u
2210	ν_R'' [b] $+\nu_2(H_2O)$	b_u
3240	$\nu_2+\nu_2(H_2O)$	b_u
3399	$\nu_1(H_2O)$	b_u
3515	$\nu_3(H_2O)$	a_u

[a] sh indicates shoulder

[b] Liberation mode. J. van der Elsken and D. W. Robinson, Spectrochim. Acta 17, 1249 (1961).

Table 2. Analysis of the Infrared Spectra of α- and β-$CaSO_4 \cdot 1/2H_2O$

Frequency (cm^{-1})		Assignment	Symmetry Species
α-$CaSO_4 \cdot 1/2H_2O$	β-$CaSO_4 \cdot 1/2H_2O$		
595	594	$\nu_4(SO_4)$	a_u
628	628	$\nu_4(SO_4)$	b_u
658	655	$\nu_4(SO_4)$	b_u
670 sh [a]	669	unassigned	-
1007	1002	$\nu_1(SO_4)$	a_u
1090	1090	$\nu_3(SO_4)$	b_u
1145	1145	$\nu_3(SO_4)$	b_u
1616	1615	$\nu_2(H_2O)$	b_u
2110	2110	$\nu_3 + \nu_1(H_2O)$	b_u
2205	2205	$\nu_{R''}$[b] $+ \nu_2(H_2O)$	b_u
3528	3528	$\nu_1(H_2O)$	
3604	3604	$\nu_2(H_2O)$	

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[a] sh indicates shoulder

[b] Liberation mode. J. van der Elsken and D W. Robinson, Spectrochim. Acta 17, 1249 (1961).

Table 3. Correlation Chart for SO_4^{2-} Infrared Active Fundamentals

Fundamental	Symmetry Species	
	T_d a/	C_{2h} a/
1	a_{1g} b/	a_u
2	e_g b/	$2a_u$
3	t_{2u}	a_u, $2b_u$
4	t_{2u}	a_u, $2b_u$

a/ Point group representation

b/ Infrared inactive, but has active component when coupled to a C_{2h} symmetry.

Table 4. Correlation Chart for Isolated and Lattice H_2O

Molecular Fundamentals of Isolated H_2O [a]	Crystal Modes of H_2O in $CaSO_4 \cdot 2H_2O$ [b]
1	a_u, b_u, a_g, b_g
2	a_u, b_u, a_g, b_g
3	a_u, b_u, a_g, b_g

a/ Belongs to the C_{2v} group.

b/ C_{2h} point group.

Table 5. Vibrational Frequencies of Free and Lattice H_2O

Molecule	Frequencies of H_2O Vibrations (cm^{-1})		
	ν_1	ν_2	ν_3
$H_2O_{(v)}$ [a]	3657	1595	3756
$H_2O_{(l)}$ [b]	3219	1627	3445
$CaSO_4 \cdot 2H_2O$ [c]	3399	1612 & 1672	3515
α- and β-$CaSO_4 \cdot 1/2H_2O$	3528	1616	3604

[a] W. S. Benedict, N. Gailar and E. K. Plyler, J. Chem. Phys. 24, 1139 (1956).

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CAPTIONS FOR FIGURES

Figure 1. The infrared spectra of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 1/2H_2O$ dispersed in KBr pellets.

Figure 2. The infrared spectra of $CaSO_4 \cdot 2H_2O$ and α- and β-$CaSO_4 \cdot 2H_2O$. Specimens prepared by the nujol mull technique. N indicates peak attributed to nujol.

Figure 3. The infrared spectrum of $CaSO_4 \cdot 2H_2O$, in a KBr pellet, heated at 109°C in an air oven.

Figure 4. Scanning electron microgram of $CaSO_4 \cdot 2H_2O$ with a magnification factor of 900.

Figure 5. Scanning electron microgram of α-$CaSO_4 \cdot 1/2H_2O$ with a magnification ratio of 1000.

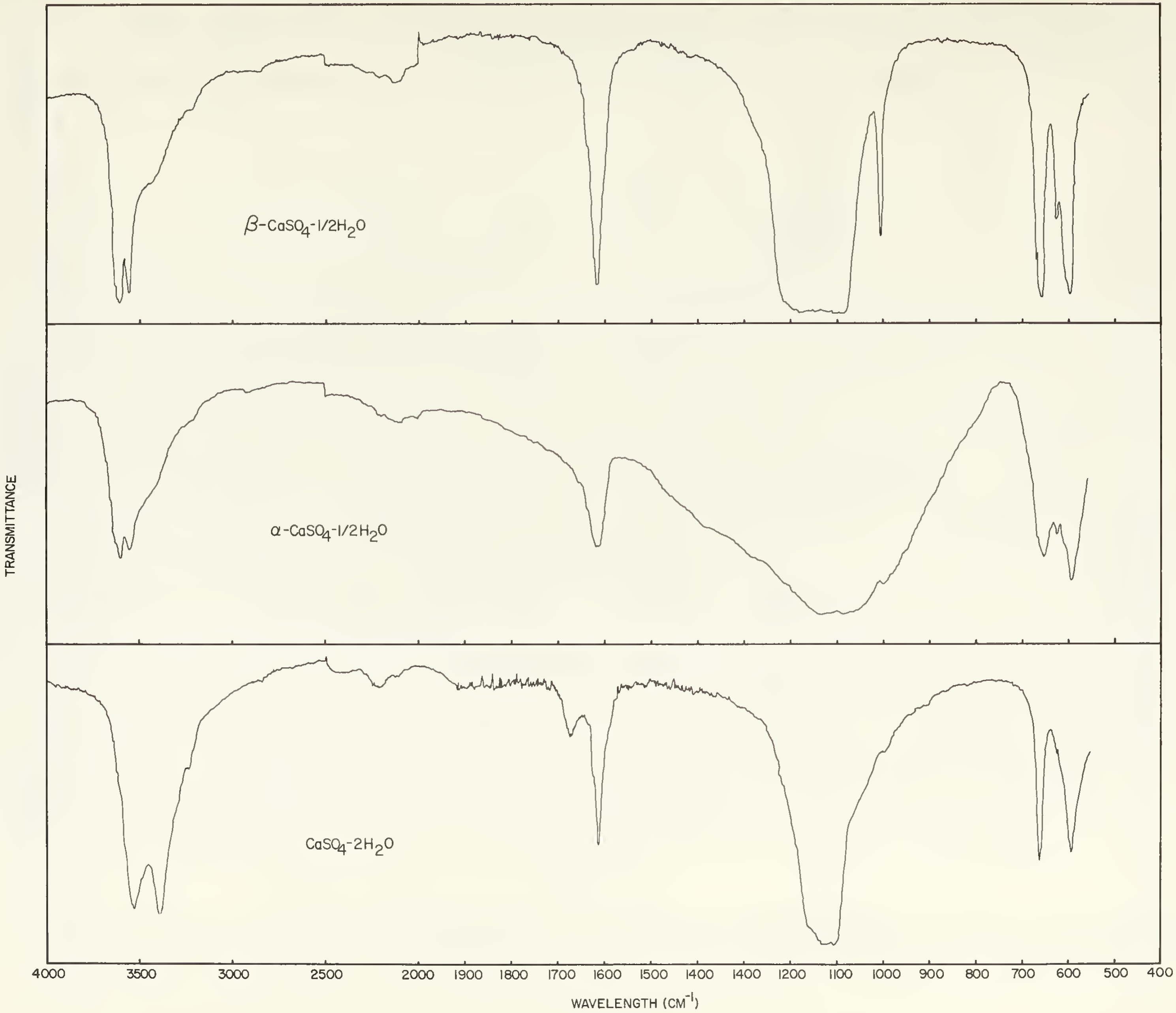
Figure 6. Scanning electron microgram of β-$CaSO_4 \cdot 1/2H_2O$ with a magnification factor of 900.

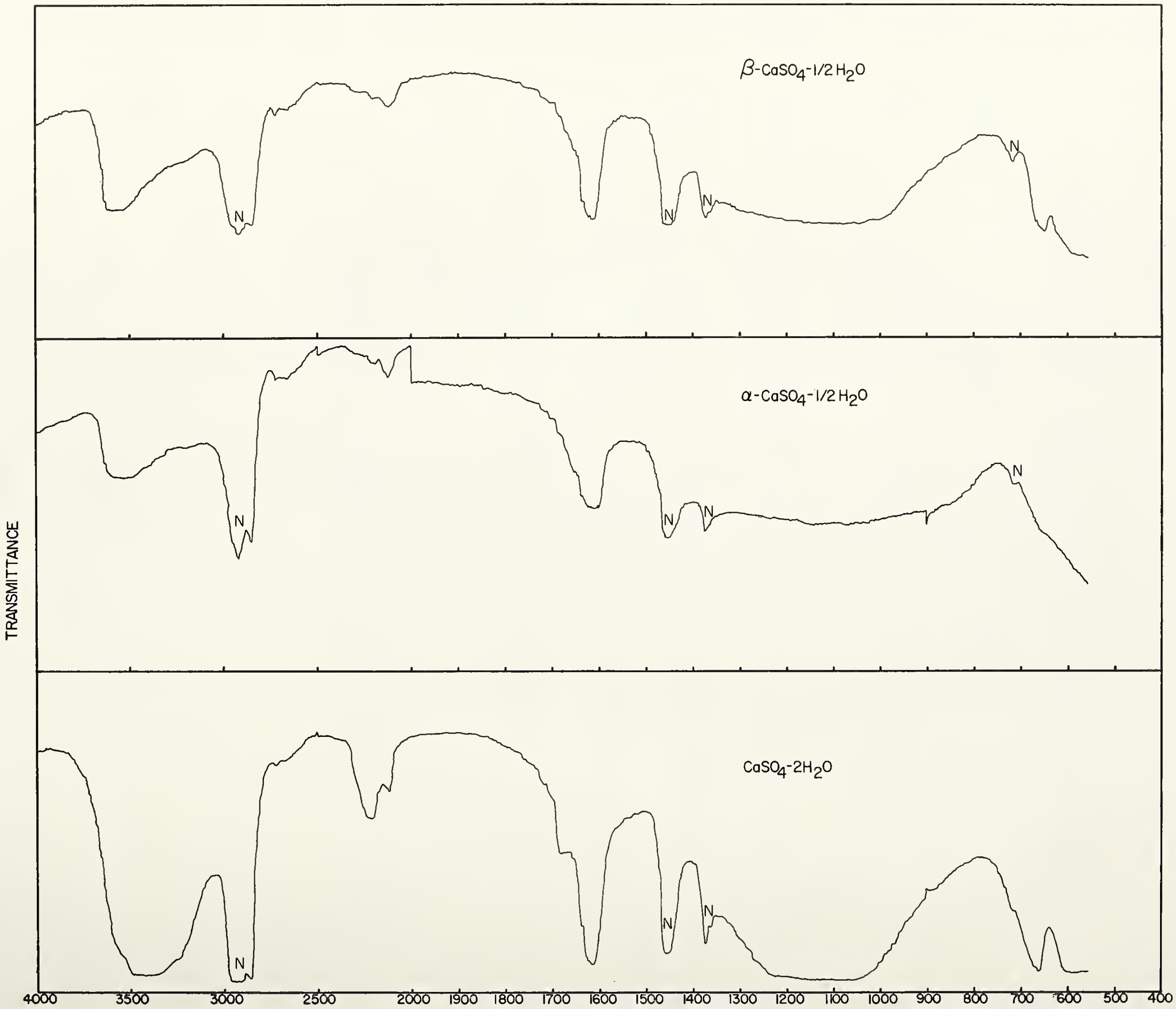
Figure 7. X-ray powder diffraction pattern of $CaSO_4 \cdot 2H_2O$.

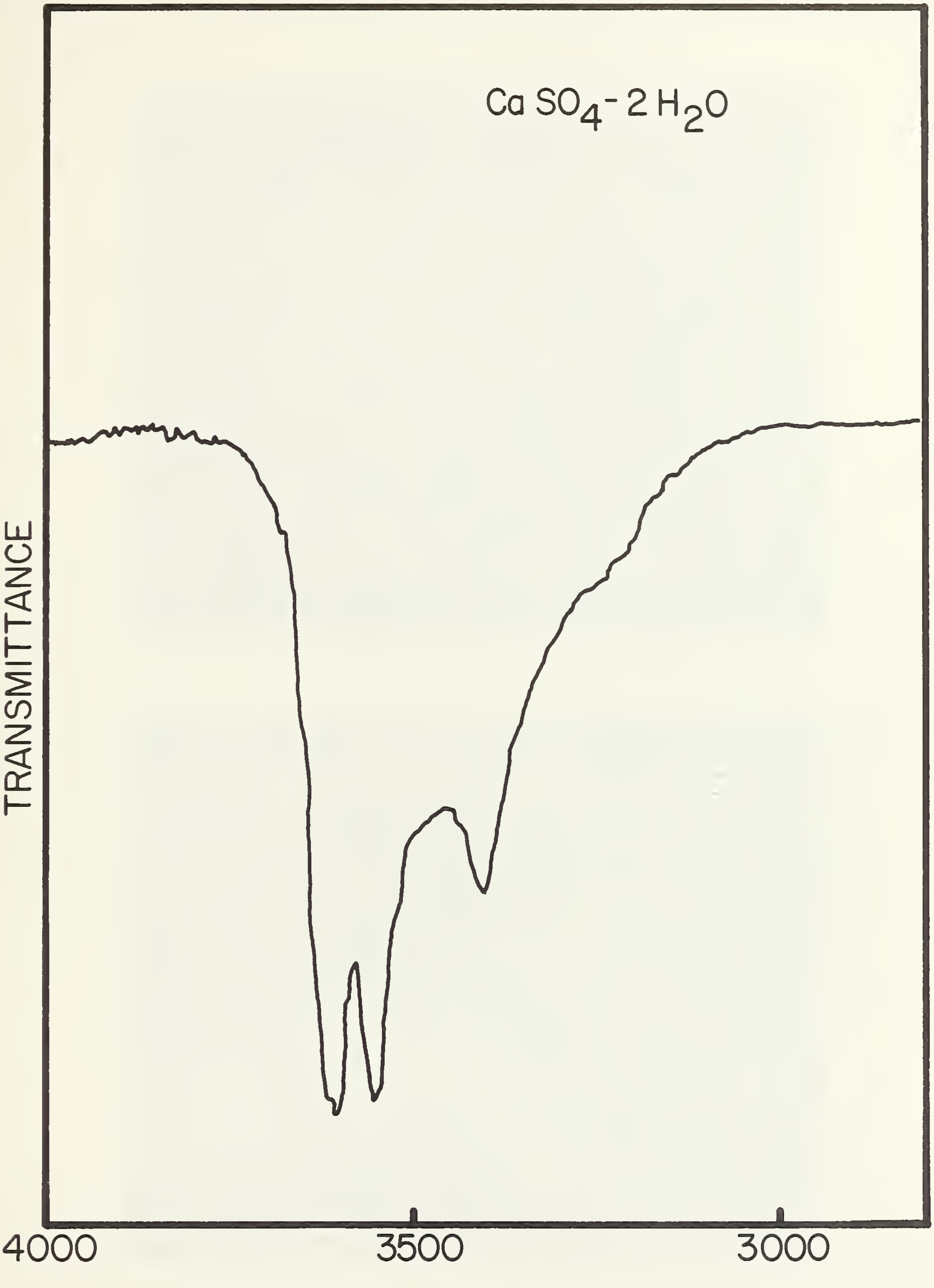
Figure 8. X-ray powder diffraction pattern of α-$CaSO_4 \cdot 1/2H_2O$.

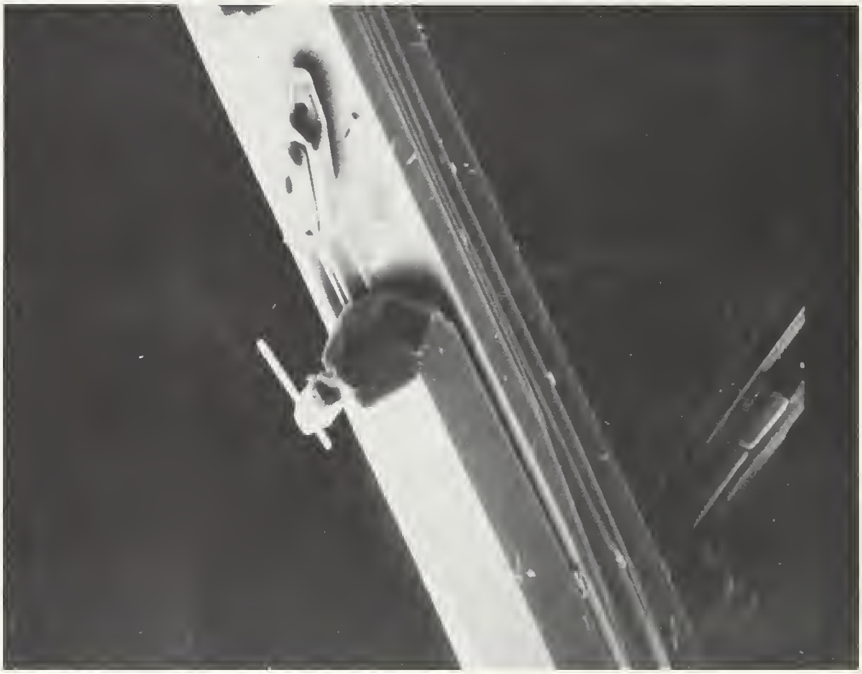
Figure 9. X-ray powder diffraction pattern of β-$CaSO_4 \cdot 1/2H_2O$.

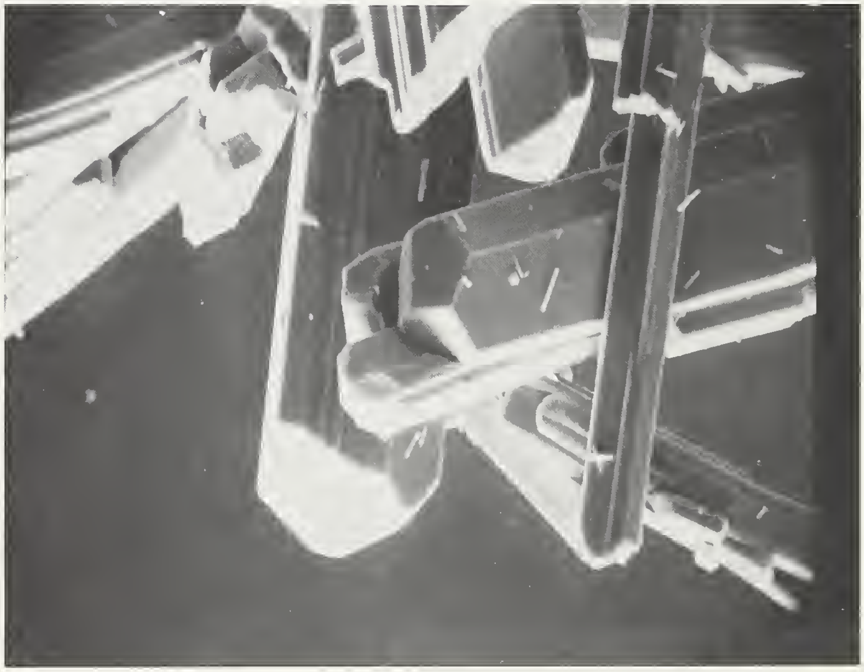
Figure 10. X-ray powder diffraction pattern with 2θ between 48 and 50° of α- and β-$CaSO_4 \cdot 1/2H_2O$, with an enlarged scale.

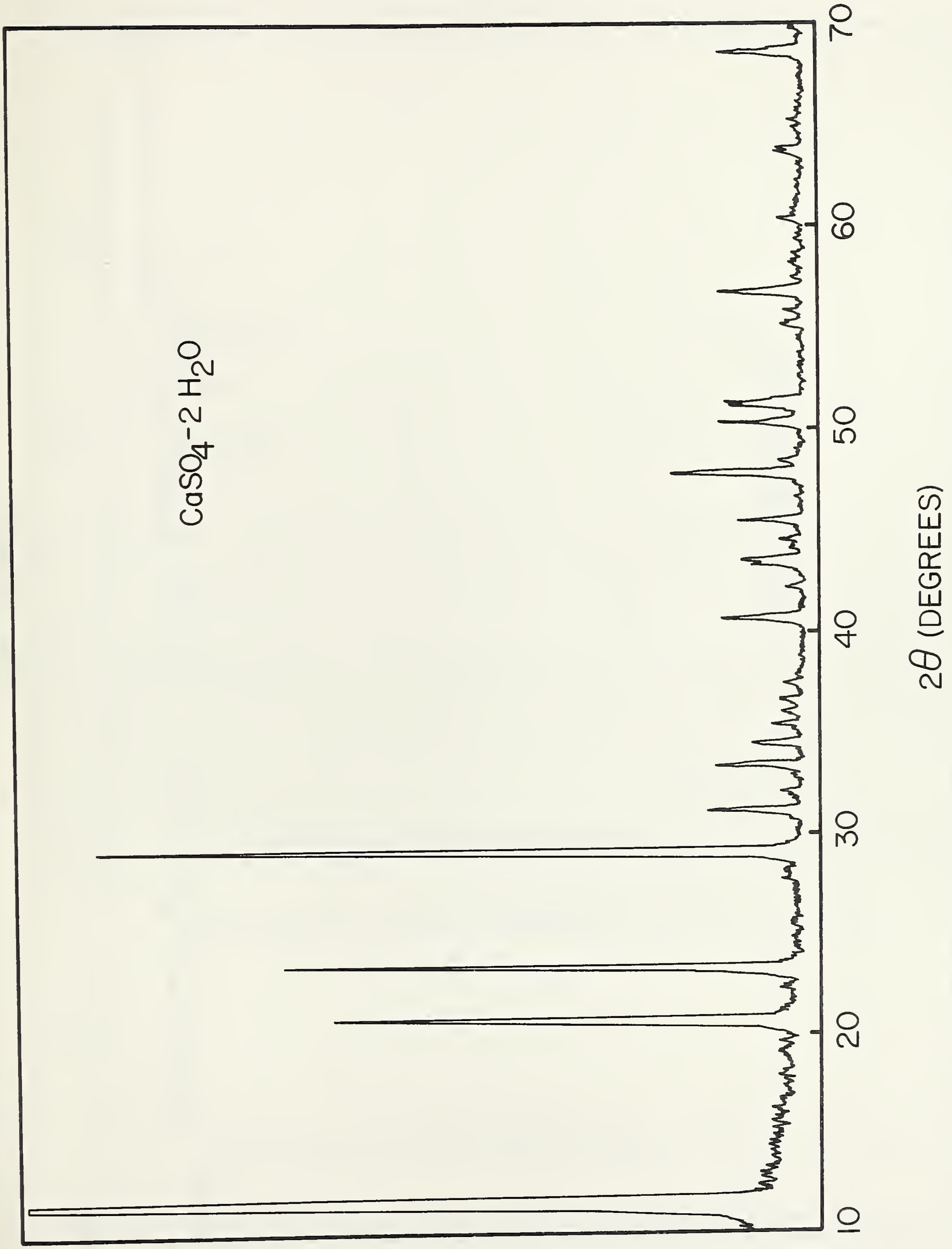

TRANSMITTANCE
β-$CaSO_4$-1/2H_2O
α-$CaSO_4$-1/2H_2O
$CaSO_4$-2H_2O
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1400
1200
1100
1000
900
800
700
600
500
400
WAVELENGTH (CM^{-1})

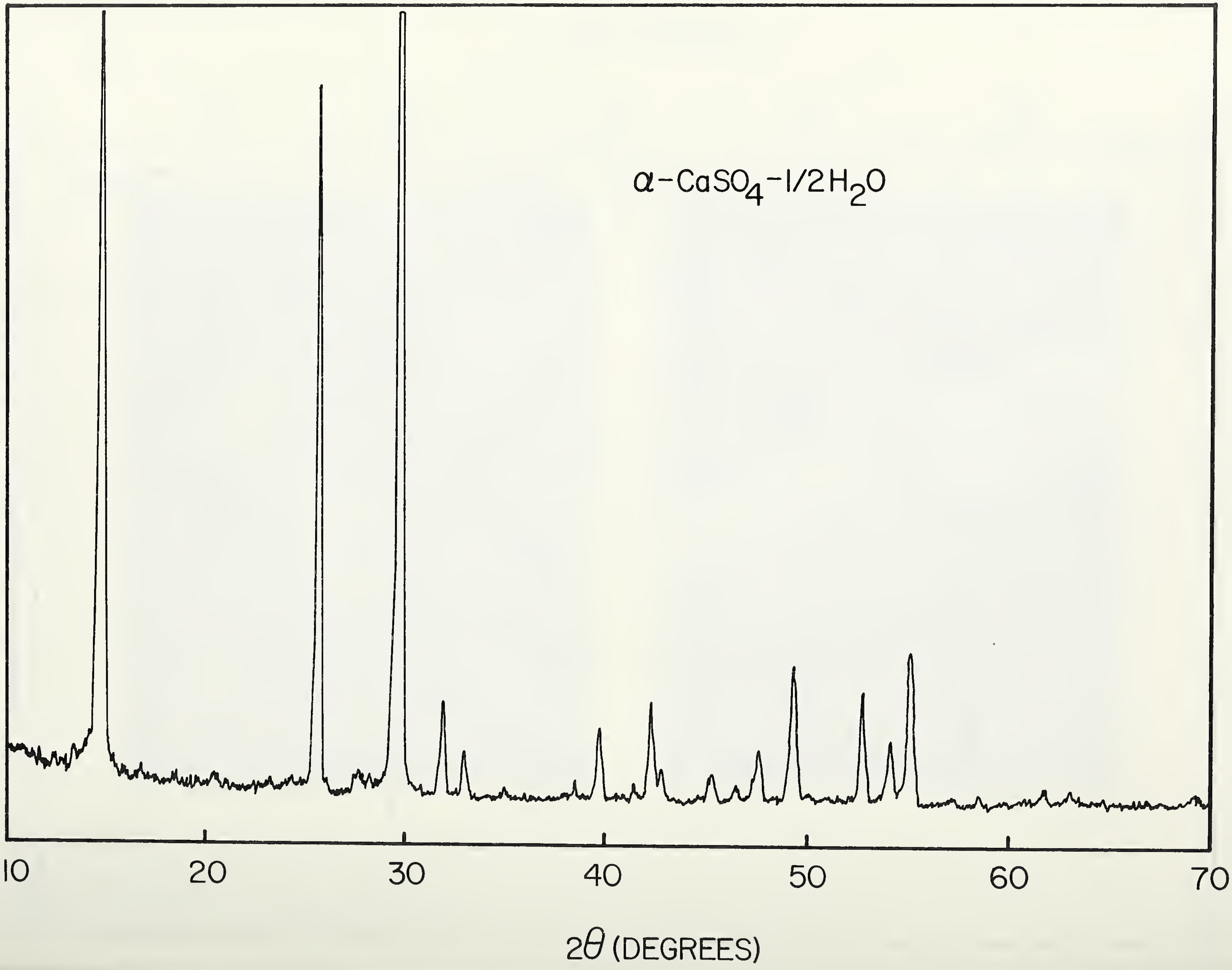

β-$CaSO_4$·1/2 H_2O
α-$CaSO_4$·1/2 H_2O
$CaSO_4$·$2H_2O$
N
TRANSMITTANCE
4000
3500
3000
2500
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400

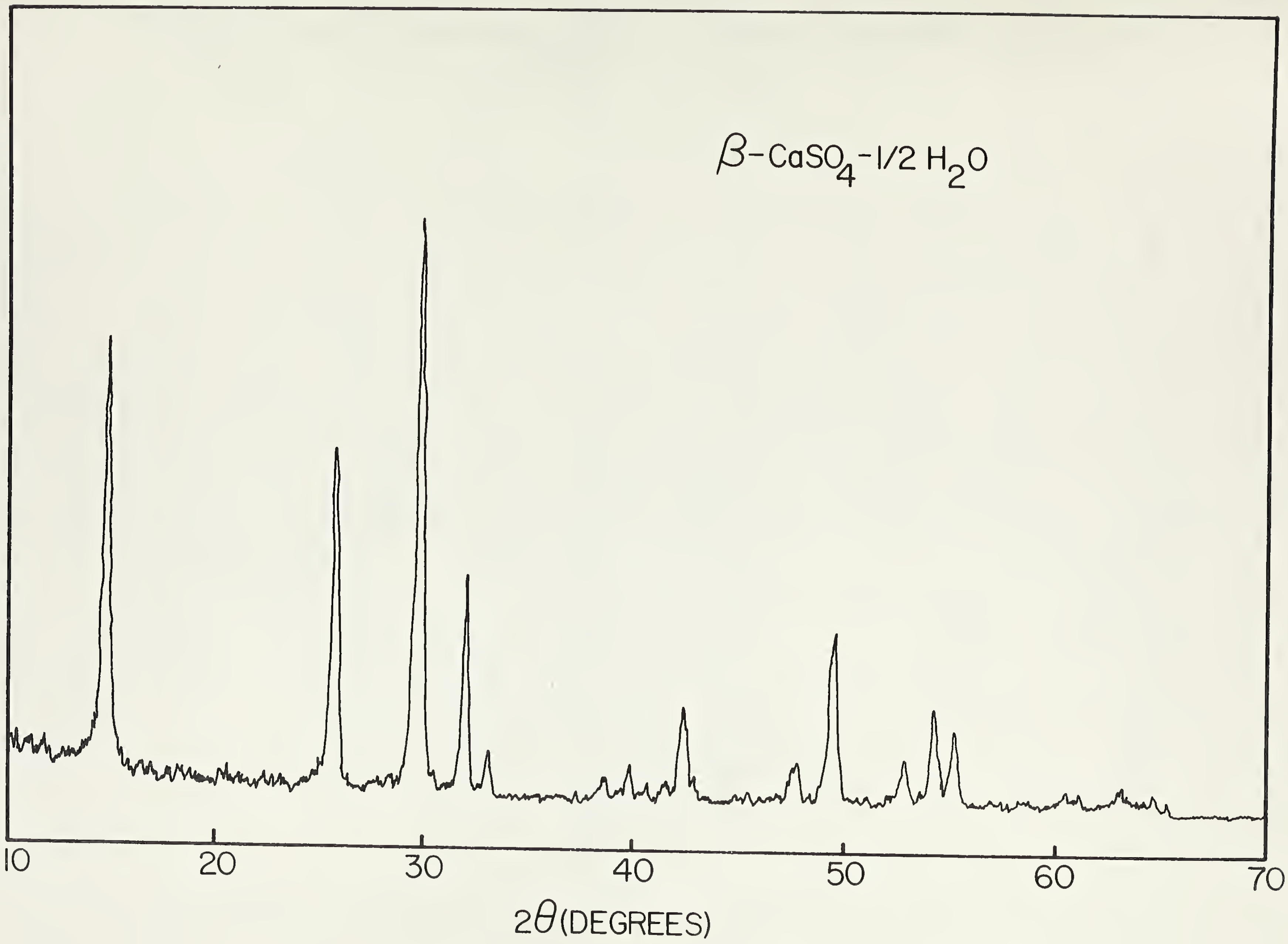

Ca SO$_4$- 2 H$_2$O
TRANSMITTANCE
4000
3500
3000
FRENQUENCY (CM^{-1})

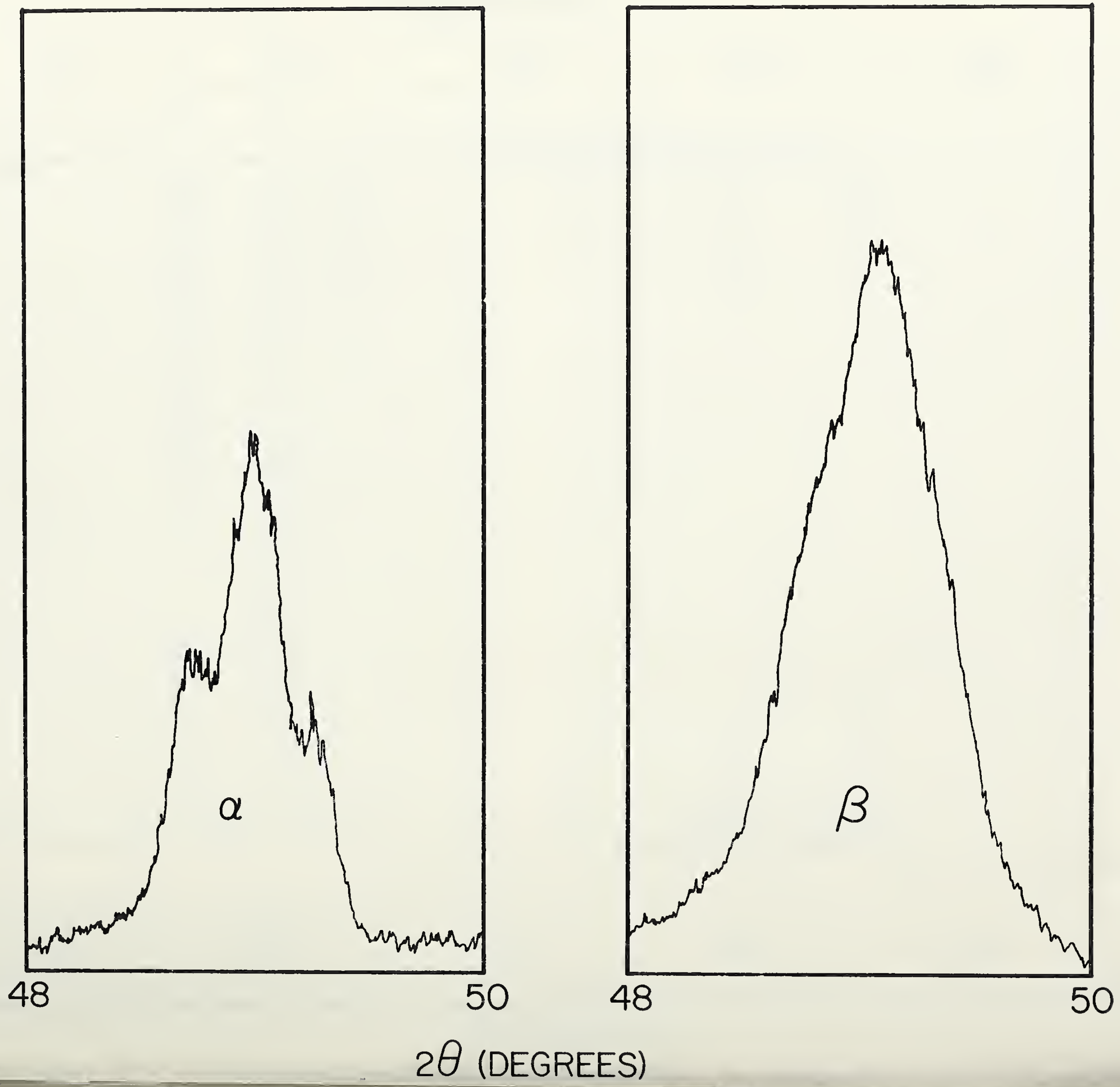


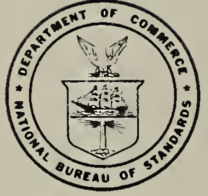



$CaSO_4$-2 H_2O
10
20
30
40
50
60
70
2θ (DEGREES)


α-$CaSO_4$-1/2H_2O
10
20
30
40
50
60
70
2θ (DEGREES)


β-$CaSO_4$-1/2 H_2O
10
20
30
40
50
60
70
2θ(DEGREES)


α
β
48
50
48
50
2θ (DEGREES)



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