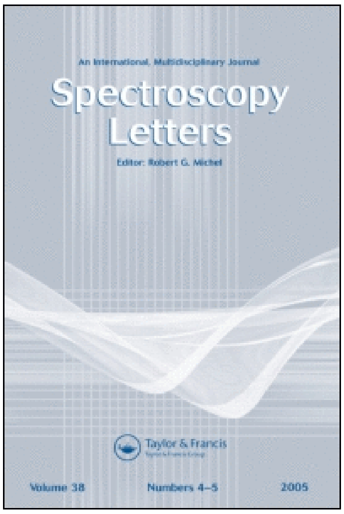

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HIGH-TEMPERATURE RAMAN SPECTRAL INVESTIGATION OF SODIUM SULFATE

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KEY WORDS: Sodium Sulfate, Raman Spectra, High Temperature, Phases

ABSTRACT

High-temperature Raman spectra were measured for sodium sulfate at various temperatures. Crystalline phases were identified at the various temperatures. Factor group and band assignment analysis were conducted for each observed phase in order to understand the vibrational nature of their Raman bands.

INTRODUCTION

Sulfate crystals can appear as inclusions in soda lime silicate glasses during various sulfur oxide treatments. Such inclusions can be related to the various crystalline phases of sodium and calcium materials. There are a significant number of crystalline structural possibilities for these sulfates. In this study, high-temperature Raman spectra were measured for sodium sulfate materials at various temperatures in order to distinguish between its various phases. Raman spectra were measured in both a heating and a cooling cycle. Particular crystalline phases were identified at various temperatures Factor group and band assignment analysis were conducted for each observed in order to better understand the vibrational nature of their Raman bands.

EXPERIMENTAL PROCEDURES

A Jobin-Yvon U1000 double monochrometer with an attached Olympus microscope was used to measure the Raman spectra. The green laser line (514.5 nm) of an argon-ion laser was used as the excitation source to measure the vibrational spectra of the crystalline material. The laser power at the entrance of the microscope was on the order of <250mW for the measurements. A photomultiplier tube was used the detector.

A platinum strip heating stage was constructed so that the vibrational Raman spectra could be obtained for the samples. The heating stage was designed so that spectra were collected in the back-scattering mode using the optical path of the Raman microprobe, but without the ability to resolve small features on the samples. The objectives were removed from the microscope assembly, and the heating stage was positioned on the microscope stage. A simple lens was used to focus the laser beam on the sample, and it also served as the collection lens to guide the Raman-scattered spectra to the spectrometer. Approximately one gram of sample was placed on the platinum heating strip. Spectra were collected at each temperature of interest. After collection of each spectrum, the temperature was increased to the next hold point, and the next spectrum was acquired.

RESULTS AND DISCUSSION

Raman spectra were investigated for crystalline sodium sulfate at various temperatures in order to help to identify the specific major crystalline sulfate phases that were present as inclusions in silicate glasses. Figures 1 and 2 illustrate measured Raman spectra that were obtained for sodium sulfate (form V) at high temperatures during its heating cycle, and then during the cooling cycles of its heated product. Phase interpretation of Raman microprobe spectral data of sodium sulfate with change in temperature is consistent with the analysis of the high-temperature dynamic x-ray diffraction data. One may note that the thenardite phase (form V) of sodium sulfate converts to the hexagonal phase (form I) upon its phase transition during the heating cycle. One may also note that the hexagonal phase converts to an orthorhombic phase (form III) during phase transition occurring in the cooling cycle. Table I lists the Raman band locations and assignments for each of the various sodium sulfate phases that were examined in this investigation.

Factor group analysis was performed on several of the sulfate phases to determine the nature of the vibrational modes in the Raman spectra. In case of free sulfate ion (SO_4^{2-}) with T_d symmetry, point group analysis predicts four fundamental vibrations: $\nu_1(A_1)$ = 981 cm^{-1} (nondegenerate), $\nu_2(E_2)$ = 451 cm^{-1} (doubly degenerate), $\nu_3(F_2)$ = 1104 cm^{-1} (triply degenerate), and $\nu_4(F_2)$ = 613 cm^{-1} (triply degenerate). Site and factor group group symmetry of the sulfate ion in the various investigated crystalline phases can be used to determine the physical nature of the measured Raman vibrational spectra. The correlation method facilitates placement of the intramolecular vibrations of the free sulfate ion into the proper site and factor group symmetries of corresponding crystal structures. This process determines the Raman activities of the internal modes of the sulfate ions in the crystal structure.

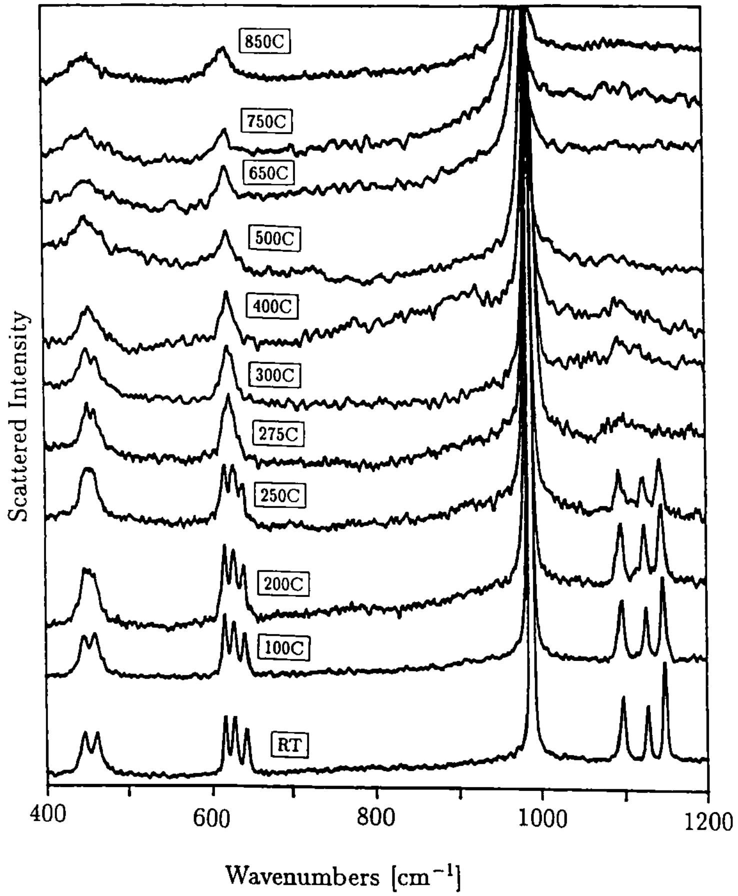

Fig. 1. Raman Spectra of Sodium Sulfate at Increasing Temperatures. Spectrum to 250C indicate Na_2SO_4 (thenardite, form V). Spectrum from 275C indicate Na_2SO_4 (form I).

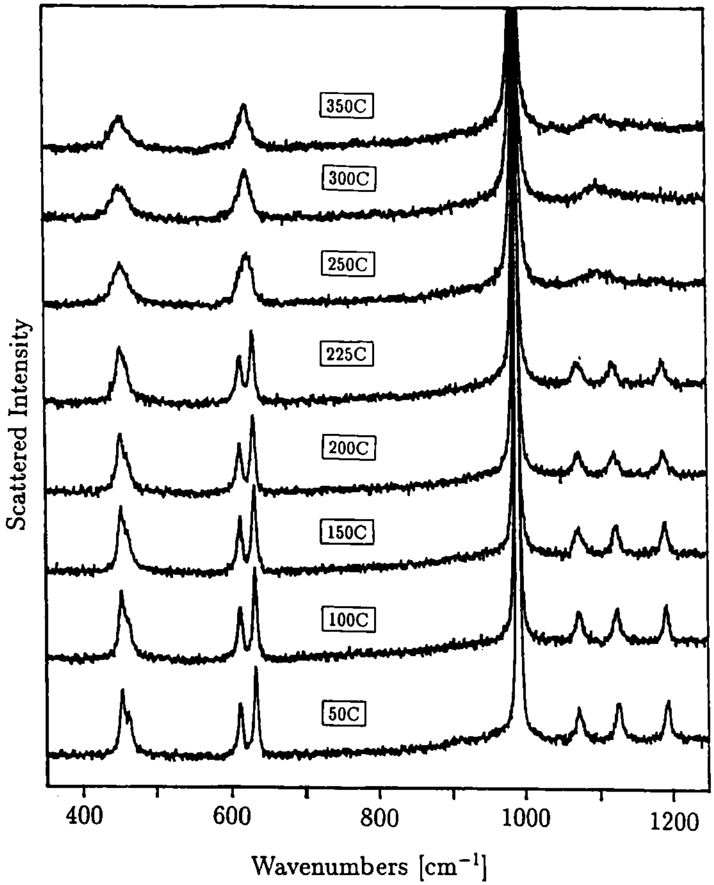

Fig. 2. Raman Spectra of Sodium Sulfate at Decreasing Temperatures. Spectrum to 250C indicate Na_2SO_4 (form I). Spectrum from 225C indicate Na_2SO_4 (form III).

Table I. Raman band locations (cm^{-1}) for sodium sulfate.

Compound	ν_1	ν_2	ν_3	ν_4
Na_2SO_4	990	448	1099	618
(thenardite)		463	1129	629
(form V)			1149	644
Na_2SO_4	992	445	1072	612
(form III)		463	1127	633
			1195	
Na_2SO_4	989	455	1100	623
(form I)				

The crystal structure of Na_2SO_4 phase (form V) possesses an orthorhombic arrangement whose space group is Fddd - D_{2h}^{24} with eight formula units per crystallographic unit cell [1]. Table II indicates the correlation diagram for the site and factor group analysis of Na_2SO_4 (form V). Factor group analysis for Na_2SO_4 (form V) predicts eighteen sulfate internal modes:

$$\Gamma = 3A_g + 2B_{1g} + 2B_{2g} + 2B_{3g} + 3A_u + 2B_{1u} + 2B_{2u} + 2B_{3u}.$$

From this set of predictions, the nine Raman-active bands are $3A_g + 2B_{1g} + 2B_{2g} + 2B_{3g}$.Also,one finds one Raman-active band for ν_1, two for ν_2, and three for both ν_3 and ν_4. Close comparison of the observed Raman spectral data for the powdered sulfate with this crystal structure with predicted results shows complete agreement.

The crystal structure of Na_2SO_4 phase (form III) also has an orthorhombic arrangement, but its space group is Cmcm - D_{2h}^{17} with four formula weights per crystallographic unit cell [2]. Table

Table II. Correlation diagram for vibrational modes of the SO_4^{2-} ion of Na_2SO_4 (form V).

Γ	ν_{vib}	Molecular Symmetry T_d	correlation	Site Symmetry D_2	c_ξ	a_ξ	correlation	Factor Group D_{2h}	c_ξ	a_ξ
2	1	A_1		A	1	2		A_g	1	1
								A_u	1	1
4	2	E		A	1	2		A_g	1	1
								A_u	1	1
				A	1	2		A_g	1	1
								A_u	1	1
12	6	F_2		B_1	1	4		B_{1g}	1	2
								B_{1u}	1	2
				B_2	1	4		B_{2g}	1	2
								B_{2u}	1	2
				B_3	1	4		B_{3g}	1	2
								B_{3u}	1	2

III indicates the correlation diagram for the site and factor group of Na_2SO_4 (form III). The factor group analysis predicts eighteen sulfate internal modes:

$$\Gamma = 4A_g + 2B_{1g} + B_{2g} + 2B_{3g} + A_u + 2B_{1u} + 4B_{2u} + 2B_{3u}.$$

Nine Raman-active bands are $4A_g + 2B_{1g} + B_{2g} + 2B_{3u}$. The analysis also predicts one Raman-active band for ν_1, two for ν_2, and three for both ν_3 and ν_4. Comparison of observed Raman spectra with the group theoretical predictions indicates that one Raman band is missing for ν_4. Choi et al.[3] performed polarized Raman spectral measurements using a single crystal of Na_2SO_4 (form III) at room temperature. Their study indicated that the band at ca. 633 cm^{-1} for ν_4 is composed of two bands which can only be distinguished with polarized Raman spectral data. The Raman spectral measurements in this study were performed on powdered samples placed on a platinum heating element, measuring nonpolarized scattered light.

Table III. Correlation diagram for vibrational modes of the SO_4^{2-} ion of Na_2SO_4 (form III).

Γ	ν_{vib}	Molecular Symmetry T_d	correlation	Site Symmetry C_{2v}	c_ξ	a_ξ	correlation	Factor Group D_{2h}	c_ξ	a_ξ
2	1	A_1		A_1	1	2		A_g	1	1
								B_{2u}	1	1
4	2	E		A_1	1	2		A_g	1	1
								B_{2u}	1	1
				A_2	1	2		A_u	1	1
								B_{2g}	1	1
12	6	F_2		A_1	1	4		A_g	1	2
								B_{2u}	1	2
				B_1	1	4		B_{3g}	1	2
								B_{1u}	1	2
				B_2	1	4		B_{1g}	1	2
								B_{3u}	1	2

The crystal structure of Na_2SO_4 (form I) has a hexagonal arrangement whose space group is $P6_3mmc - D_{6h}^4$ with two formula units per crystallographic unit cell[4].The usual site or factor group analysis is not possible for this phase because the site group (D_{3h}) that is available for sulfate ion in this structure is not a subgroup of the free ion group (T_d), indicating the presence of disorder in the crystal structure. The actual site symmetry of a sulfate ion on a site in the crystal is probably C_{3v}. The correlation method fails for such structures that contain disorder. The observed Raman spectra of powdered Na_2SO_4 (form I) indicates only four vibrational bands. Orientational disorder of the sulfate ions in this phase causes the resulting Raman spectra to possess broadened bands (as compared to the other sodium sulfate phases) which may arise due to disordered ion-ion interactions. The free sulfate ion with T_d symmetry has four fundamental modes of vibration.The observed Raman spectrum indicates that the nature of the site symmetry of the sulfate group in this crystal structure possesses a relationship to the free ion symmetry with the ion-ion interactions that generates broadened features with respect to the free ion's spectrum.

CONCLUSIONS

The following conclusions can be made pn the basis on this investigation:

1.) In-situ Raman spectra can be obtained at high temperatures for sodium sulfate materials which generate phase information using either heating or cooling cycles.
2.) Observed in-situ Raman spectra of powdered Na_2SO_4 (form V) is consistent with respect to the related factor group analysis.
3.) One less Raman-active band is observed for ν_4 in the spectrum for powdered Na_2SO_4 (form III). This lack is due to the overlap of two factor group-split bands which can not be detected in the nonpolarized Raman spectra of the powdered sample.
4.) Raman bands of powdered Na_2SO_4 (form I) are broadened due to disorder in the crystal structure.

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