

FTIR study of second group iodate crystals grown by gel method

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Abstract: The crystals of Strontium iodate, Zinc iodate and Mercuric iodate were grown by a simple gel method using diffusion technique. The optimum growth conditions were established by varying various parameters such as pH of the gel solution, gel concentration, gel setting time, concentrations of reactants etc. The crystals were characterized using FTIR.

Keywords: Gel technique, Strontium iodate, Zinc iodate and Mercuric iodate crystals, FTIR.

I. Introduction

The growth of single crystals in gel at an ambient temperature, which are sparingly soluble in water, is a fascinating alternative to the techniques involving high temperature and expensive equipments. During the last few years, successful application of gel growth technique has been demonstrated by the preparation of single crystals of alkaline earth metal iodate. The gel growth technique appeared quite attractive for growing crystals of such compounds on account of its unique advantages in terms of crystals produced and the simplicity of process. Crystals of iodate exhibit nonlinear optical properties and piezoelectric properties. Nonlinear optical phenomenon have found a wide variety of applications in many areas of modern science, technology and engineering. The nonlinear devices find large applications in optical communication, image processing, and wave-guide coupling.

A variety of crystals required for the purpose of research and application can be grown in silica gels. The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional crucible which permits the reagents to diffuse at a desirable controlled rate. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth.

In the present work, Second group iodate crystals were grown by gel technique using diffusion method. Optimum growth conditions for crystals were determined. Optimum conditions were established by varying various parameters such as pH of gel, gel reactants, concentration programming, effect of neutral gel etc.

II. Materials and Method

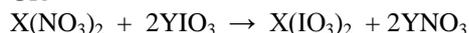
Test tubes were used as crystallizing vessels. The silica gel was used as a growth media. Gel was prepared by using glacial acetic acid and sodium meta silicate having different pH values. The chemicals used for growth of single crystals of zinc iodate were CH_3COOH ; $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$; KIO_3 , NaIO_3 ; SrCl_2 ; $\text{Sr}(\text{NO}_3)_2$; ZnCl_2 ; $\text{Zn}(\text{NO}_3)_2$; HgCl_2 ; $\text{Hg}(\text{NO}_3)_2$. All chemicals were of AR grade.

Different molar masses were tried to determine the optimum growth conditions. One of the reactants having different concentrations was incorporated into the gel. This solution was then transferred to borosil glass tube of diameter, 2.5 cm and 25 cm in height. The mouth of the tube was covered by cotton plug. After setting of the gel, it was left for aging for different periods of time. Another reactant having different concentrations was then added as supernatant over the set gel. Experiments were carried out by changing different concentrations of the reactants.

The chemical reaction inside the gel can be expressed as



OR



Where X = Sr, Zn and Hg and Y = K or Na.

III. Results and discussions

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. The technique when coupled with intensity measurements may be used for quantitative analysis. One of the most advantages of infrared spectroscopy over the usual methods of structural analysis is that it provides useful information about the structure of molecules quickly without tiresome evaluation methods. This method solved many problems in organic chemistry and co-ordination chemistry, while in some other problems infrared data advantageously complement the results obtained by other methods.

A new method known as Fourier Transform Infrared Spectroscopy (FT-IR) has come in to use more recently. It is more advanced stage of infrared spectroscopy. It gives more detailed information about the absorption bands due to presence of water molecules, metal ions, hydroxyl ions, organic molecules, etc.

Light covering the whole frequency range, typically $4000 - 400 \text{ cm}^{-1}$, is split in to two beams. Either one beam is passed through the sample, or both the beams are passed, but one beam is made to traverse longer path than the other does. Recombination of the two beams produces an interference pattern that is the sum of all the interference patterns created by each wavelength in the beam. By systematically changing the difference in the two paths, the interference patterns change to produce a detected signal varying with optical path difference. This pattern is known as interferogram, and looks nothing like a spectrum. However, Fourier transformation of the interferogram, converts it in to a plot of % transmittance against wave number, which resembles the usual spectrum obtained by traditional method. There are several advantages of FT-IR over the traditional method. Because it is not necessary to scan each wave number successively, the whole spectrum is measured in at most a few seconds. Moreover, because it is not dependent upon a slit and a prism or grating, high resolution in FT-IR is easier to obtain without sacrificing sensitivity.

FTIR of gel grown Second group iodate crystals were recorded using SHIMADZU spectrophotometer at the Department of chemistry, University of Pune. The IR spectrum was recorded in the wave number range $400-4000 \text{ cm}^{-1}$ for KBr line. The FT-IR spectrum of the strontium iodate, zinc iodate and mercuric iodate crystals are as shown in the figures 1, 2 and 3 respectively.

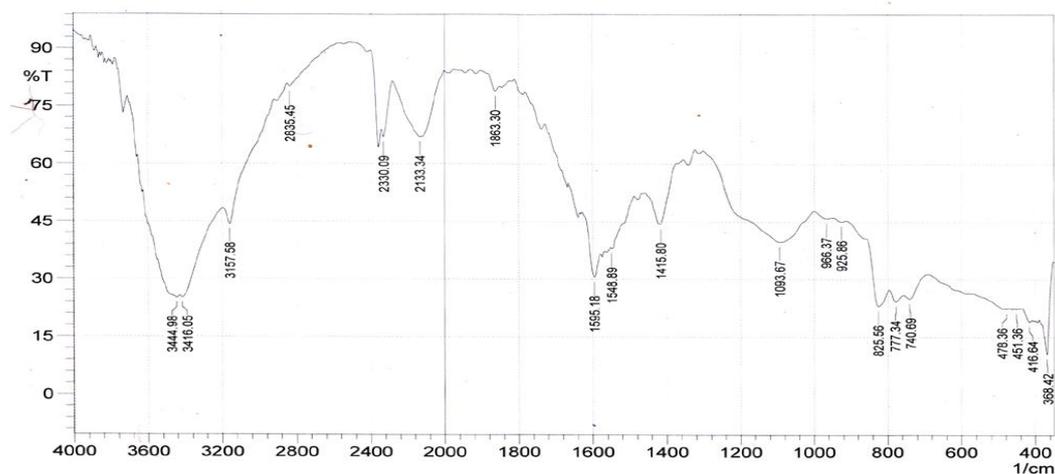


Figure 1. FT-IR spectrum of strontium iodate

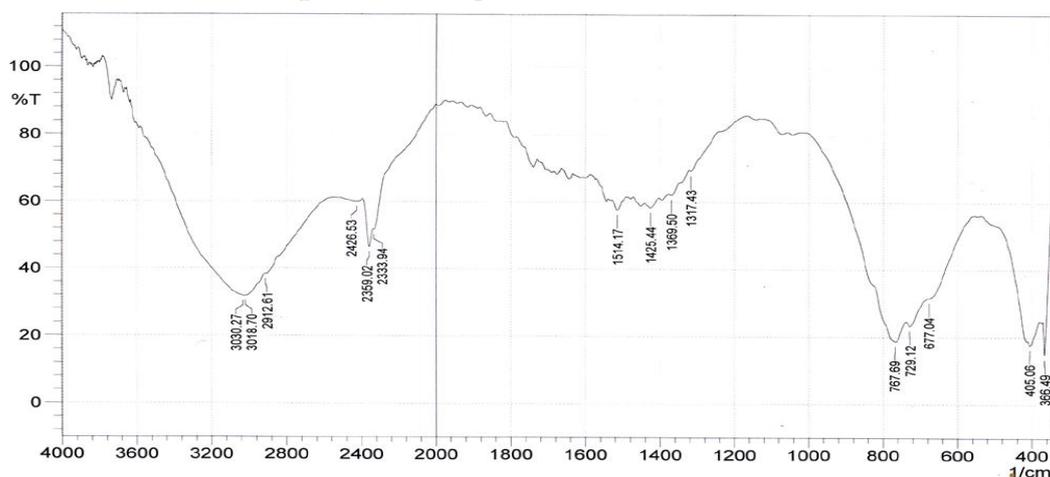


Figure 2. FT-IR spectrum of Zinc iodate

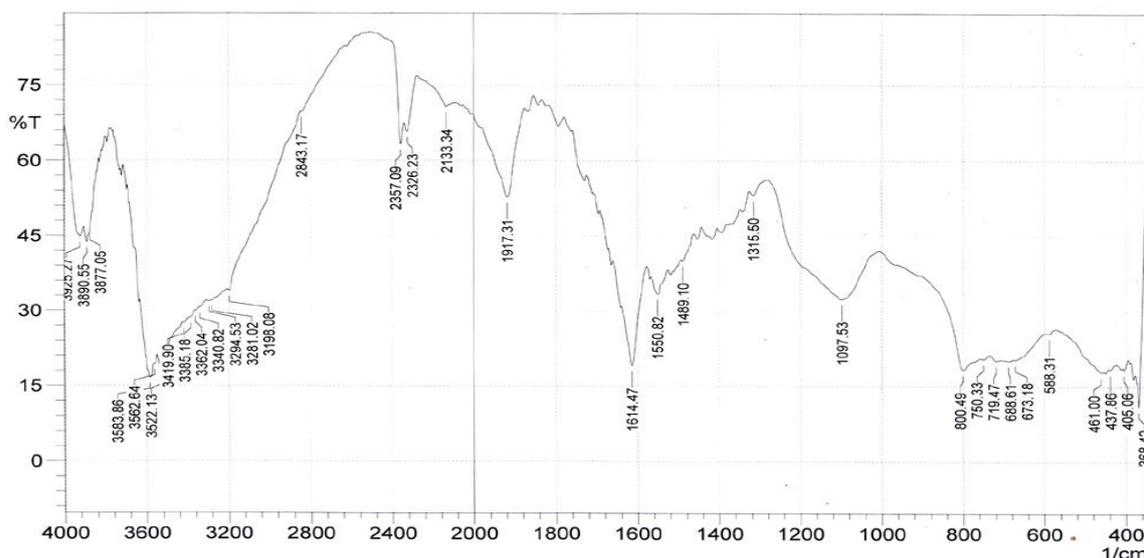


Figure 3. FT-IR spectrum of Mercuric iodate

The fundamental frequencies of the pyramidal iodate ions as have been reported earlier by Nassau et al, Dasent and Waddington, Balicheva and petrova, Sanyal and Nag, Nyquist and Kagal, are in good agreement with the observed values in the present investigation. The various bands observed in the FT-IR analysis of these crystals are shown in the table 1.

Table 1: Vibrational infrared frequencies:

Fundamental frequencies	Strontium iodate (cm ⁻¹)	Zinc iodate (cm ⁻¹)	Mercuric iodate (cm ⁻¹)
Symmetric stretching frequency, ν_1	740.69	767.69	688.61
Asymmetric stretching frequency, ν_2	478.36	405.06	461.00
Symmetric bending frequency, ν_3	825.56	729.12	800.49
Asymmetric bending frequency, ν_4	368.42	366.49	368.42

The various bands observed in the FT-IR analysis of the iodate crystals are as follows:

1. Strontium iodate:-

- i. The bands at 3416.05 cm⁻¹ and 3444.98 cm⁻¹ are due to O – H stretching with shoulder near 3157.58 cm⁻¹ due to overtone.
- ii. The bands at 1548.89 cm⁻¹ and 1595.18cm⁻¹ are due to H – O – H bending.
- iii. The bands due to vibrations involving metal, iodine and oxygen atoms are found predominantly in the range 740-830 cm⁻¹.
- iv. The fundamental frequencies of the pyramidal iodate ions are observed,
 - a. Symmetric stretching γ_1 at 740.69 cm⁻¹.
 - b. Symmetric bending γ_2 at 478.36 cm⁻¹.
 - c. Asymmetric stretching γ_3 at 825.56 cm⁻¹.
 - d. Asymmetric bending γ_4 at 368.42 cm⁻¹.
- v. The extra bands observed in the range 400-480 cm⁻¹ may be due to metal – oxygen vibration.
- vi. One more extra band observed in the range 740-830 cm⁻¹ may also be due to vibration between metal – iodine – oxygen atoms.

The bands due to vibration involving metal, iodine and oxygen atoms are found predominantly in the range 740-830 cm⁻¹. The fundamental infrared frequencies, observed in all iodate compounds in general, are also found in the present FT-IR analysis, which confirm the iodate group of grown crystals. The bands at 368.42 cm⁻¹ are due to the iodate group. The dominant absorption bands are found at 700-825 cm⁻¹ in all iodate compounds (Nakamoto 1970) and can be expected to contain ν_1 , ν_3 as well as possible splitting of ν_3 . From the spectral analysis, it is clear that in case of strontium iodate crystals, the bands at 3157 cm⁻¹, 3416 cm⁻¹, 3444 cm⁻¹, 1548 cm⁻¹ and 1595 cm⁻¹ are due to inclusion of one water molecule.

2. Zinc iodate:-

- vii. The bands due to vibrations involving metal, iodine and oxygen atoms are found predominantly in the range 675-770 cm⁻¹.

- viii. The fundamental frequencies of the pyramidal iodate ions are observed,
- Symmetric stretching γ_1 at 767.69 cm^{-1} .
 - Symmetric bending γ_2 at 405.06 cm^{-1} .
 - Asymmetric stretching γ_3 at 729.12 cm^{-1} .
 - Asymmetric bending γ_4 at 366.49 cm^{-1} .
- ix. The extra bands observed in the range $400\text{-}480\text{ cm}^{-1}$ may be due to metal-oxygen vibration.
- x. One more extra band observed in the range $740\text{-}830\text{ cm}^{-1}$ may also be due to vibration between metal – iodine – oxygen atoms.
- xi. All other extra bands observed in the spectra are may be due to inclusion of sodium meta silicate in the grown crystals.

The bands due to vibration involving metal, iodine and oxygen atoms are found predominantly in the range $670\text{-}770\text{ cm}^{-1}$. The fundamental infrared frequencies, observed in all iodate compounds in general, are also found in the present FT-IR analysis, which confirm the iodate group of grown crystals. The bands at 366.49 cm^{-1} are due to the iodate group. The dominant absorption bands are found at $600\text{-}800\text{ cm}^{-1}$ in all iodate compounds (Nakamoto 1970) and can be expected to contain ν_1, ν_3 as well as possible splitting of ν_3 .

3. Mercuric iodate:-

- xii. The bands observed in the range 3281.02 cm^{-1} to 3583.86 cm^{-1} are due to O – H stretching with shoulder near 3198.08 cm^{-1} due to overtone.
- xiii. The bands at 1489.10 cm^{-1} , 1550.82 cm^{-1} and 1614.47 cm^{-1} are due to H – O – H bending.
- xiv. The bands due to vibrations involving metal, iodine and oxygen atoms are found predominantly in the range $670\text{-}800\text{ cm}^{-1}$.
- xv. The fundamental frequencies of the pyramidal iodate ions are observed,
- Symmetric stretching γ_1 at 688.61 cm^{-1} .
 - Symmetric bending γ_2 at 461.00 cm^{-1} .
 - Asymmetric stretching γ_3 at 800.49 cm^{-1} .
 - Asymmetric bending γ_4 at 368.42 cm^{-1} .
- xvi. The extra bands observed in the range $400\text{-}461\text{ cm}^{-1}$ may be due to metal – oxygen vibration.
- xvii. Extra bands observed in the range $670\text{-}800\text{ cm}^{-1}$ may also be due to vibration between metal – iodine – oxygen atoms.

The bands due to vibration involving metal, iodine and oxygen atoms are found predominantly in the range $670\text{-}800\text{ cm}^{-1}$. The fundamental infrared frequencies, observed in all iodate compounds in general, are also found in the present FT-IR analysis, which confirm the iodate group of grown crystals. The bands at 368.42 cm^{-1} are due to the iodate group. The dominant absorption bands are found at $700\text{-}825\text{ cm}^{-1}$ in all iodate compounds (Nakamoto 1970) and can be expected to contain ν_1, ν_3 as well as possible splitting of ν_3 . From the spectral analysis, it is clear that in case of mercuric iodate crystals, the bands at 3198.08 cm^{-1} , 3281.02 cm^{-1} , 3294.53 cm^{-1} , 3340.82 cm^{-1} , 3362.04 cm^{-1} , 3385.18 cm^{-1} , 3419.90 cm^{-1} , 3522.13 cm^{-1} , 3562.64 cm^{-1} , 3583.86 cm^{-1} , 1550.82 cm^{-1} and 1614.47 cm^{-1} are due to inclusion of half water molecule.

IV. Conclusions

From the above studies we observe that

- Gel growth technique is suitable for growing iodate crystals.
- Different habits of these crystals can be obtained by changing parameters like gel density, gel aging, pH of gel, Concentration of reactants etc.
- Existence of Water of crystallization present in the grown crystals is confirmed by FT-IR analysis.
- Fundamental infrared frequencies observed in all iodate compounds in general, are also found in the present FT-IR analysis.

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