

Research Article

Comparative Study of Pure and Doped Single Crystals of Lead Iodide Dihydrate and Lead Tartrate Dihydrate Grown in Silica Gel Using Fourier Transform Raman Spectra

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It is presented the FT-Raman spectroscopic investigation of the lead tartrate dihydrate and lead iodide dihydrate. The difference in the spectroscopic behavior of these salts were found which can be attributed to a different geometry of the tartrate and iodide ions. The structural differences between the coordination environments of lead atoms are discussed in connection with Raman frequencies. The compounds have been synthesized using sodium metasilicate gel at ordinary temperature and pressure.

1. Introduction

Lead iodide (PbI_2) is a very important material with a technological applicability as a room temperature detector. It is a wide-band-gap semiconductor ($E_g > 2$ eV) with high environmental stability efficiency [1–5]. Recently, its band-gap energy and thermal properties were determined by photo acoustic spectroscopy [5, 6]. The electronic and optical properties of lead iodide have been investigated experimentally by means of optical absorption and spectroscopic ellipsometry, and theoretically by a full-potential linear muffin-tin-orbital method [7, 8], PbI_2 has been recognized as a very promising detector material with large technological applicability [9]. The single crystals of lead iodide have been grown by gel method. The observations of the faces of these crystals revealed that they have grown layer-by-layer as well as spiral mechanisms [7, 8, 10, 11]. In order to study the electronic structure of PbI_2 [11–15], the spin-orbit coupling was included. The dielectric function was calculated in the momentum representation [16–18]. From the literature survey shows that there is a very small anisotropy in the optical properties of PbI_2 [17–22]. The triangular growth spirals, which are not clearly resolved. But these triangular spirals are seen to be oriented at the site of triangular etch pits

produce during the growth processes [23–25]. In fact there is an interlocking of spirals which are oriented anticlockwise and clockwise direction. Lead tartrate initially grew as dendrites because of the large latent heat of crystallization and poor ionic conductivity [26]. The phenomenon of transformation of dendrites into single crystals indicates that it may be useful in the growth of single crystals of materials which normally grow as dendrites. It is now well-established that surface energy and surface diffusion are decisive factors on the shape stability of spherical particles. But the reduction in size is remarkable in the case of cadmium doped crystals.

2. Experimental

2.1. Synthesis of Lead Iodide Single Crystals. Dissolve 244 g of sodium metasilicate in 500 mL of double distilled water to obtain the stock solution 7.5 mL of stock solution is diluted with equal quantity of water. Then 15 mL of 2 M acetic acid and 6 ml of 1 M lead acetate are combined, with continued agitation. The mixture is allowed to set, and 20 mL of 0.75 M potassium iodide are then placed on the top of gel without any disturbances. Good hexagonal plates of lead iodide grow within about three weeks with deep yellowish and luminescent in nature. Zinc acetate is used as dopant

TABLE 1: Comparative study on the spectral datas of $\text{PbI}_2 \cdot 2\text{H}_2\text{O}$ & $\text{PbC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$.

| Pure PbI_2 Bands cm^{-1} | Doped PbI_2 bands cm^{-1} | Assignment of bands | Pure $\text{PbC}_4\text{H}_4\text{O}_6$ bands cm^{-1} | Doped $\text{PbC}_4\text{H}_4\text{O}_6$ bands cm^{-1} | Assignment of bands |
|--|---|--|---|--|---|
| 3012 | 3254 | OH stretching | 2965 | 2940 2918 | asymmetric and symmetric stretch of C–H |
| 2515 | 2516 | O–H torsional | 1598 | 1574 | H–O–H bending, |
| 2336 | 2335 | mode and | 1419 | 1440 | O–H torsional mode |
| 2312 | 2310 | interaction with | 1299 | 1392 | |
| 2267 | 2267 | other molecule with interaction between the hydroxyl group | 1236 | 1308 | Fermi Resonance producing splitting of carbonyl group |
| 2243 | 2221 | The splitting provides | 1124 | 1276 | |
| 2122 | 2184 | direct insight into the | 1066 | 1240 | |
| 2078 | 2077 | structure of hydrogen | 1005 | 1120 | C–O stretch coupled with |
| 2062 | 2062 | bonds and into process of | 927 | 1078 | in-plane bending of C–H |
| 2030 | 2034 | bond formation and cleavage | 901 | 1002 | mode |
| | | O–D stretch | 820 | 894 | |
| | | | 718 | 829 | |
| | | | 597 | 806 | |
| | | | 549 | 710 | C–O–H and –C=O group bending |
| | | | 430 | 618 | |
| | | | 323 | 642 | |
| | | | 276 | 506 | |
| | | | 172 | 438 | C=O stretching band |
| | | | | 311 | |
| | | | | 290 | OH torsional mode |
| | | | | 260 | out-of plane bending of |
| | | | | 198 | C–O–H |
| | | | | 168 | The bond correlated with |
| | | | | 142 | out-of-plane bending mode |
| | | | | 123 | of C–O–H |
| | | | | | out-of-plane bending mode |
| | | | | | of hydrogen bonding |

for doping the lead iodide crystals. The first reports of light effects on nucleation in solution date from 1900, and similar effects in gels have also been reported from time to time [23, 40]. The chemistry, involved in the following processes:



The appearance of “zigzags” yellowish crystals as shown in Figure 1 could be viewed through the boiling test tube. In this note we report our own results of a Raman study of a single crystal of lead iodide, the assignment of Raman frequencies involving mainly motion of lead ions and modes involving mainly halogen ions [26]. Some surface barrier properties of lead iodide crystals are reported in physica status solidi(a). The barrier layer at a free surface of a PbI_2 crystal surrounded by a non polar gas has been found to exhibit pronounced voltage rectification when passed by an alternating current of

constant amplitude. The light induced relaxation of ν_s has a half-life time $\tau_{1/2} = \tau_0^{\exp u/kT}$, where u is the activation energy [27]. Optical properties of lead iodide are reported in [28, 29] reports the third order nonlinear optical characteristics of new chalcogenide glass containing lead iodide.

2.2. Lead Tartrate Dihydrate Single Crystal Synthesis. In the present experiment, the possible reaction is $\text{Pb}(\text{NO}_3)_2 + \text{C}_4\text{H}_6\text{O}_6 \rightarrow \text{PbC}_4\text{H}_6\text{O}_6 + 2\text{HNO}_3$.

In about an hour, a white color diffused from the top of the gel to the lower regions [26] of the gel of pH4.5. After 10 days, the precipitates extended to a depth of 6.3 cm from the gel surface as shown in Figure 2 were assigned on the basis of the characteristic vibrations of $(\text{C}_4\text{H}_4\text{O}_6)^{2-}$ ion and H_2O . A free tartrate ion in zigzag planar configuration has C2 symmetry. The $(\text{C}_4\text{H}_4\text{O}_6)^{2-}$ consists of two halves,



FIGURE 1: Synthesis of lead iodide single crystals.

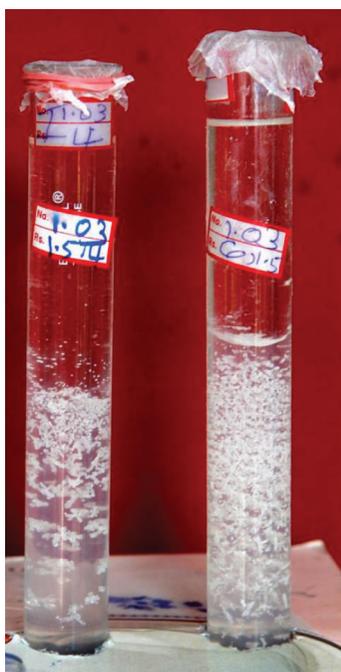


FIGURE 2: Synthesis of lead tartrate single crystals.

each half consisting of a carboxylic group tetrahedral carbon and hydroxyl oxygen, the halves are bridged through bonds. The multiplicity of Raman stretching bands suggests the presence of at least two crystallographically distinct water molecules in the hydrated compounds. The phenomenon of transformation of dendrites into single crystals of lead tartrate indicates that it may be useful in the growth of single crystals of materials which normally grow as dendrites. It is now well established that surface energy and surface diffusion are decisive factors on the shape stability of spherical

particles [30]. But the reduction in size is remarkable in the case of cadmium doped crystals. The dendritic growth of lead tartrate in gel media is already reported by [27].

3. Result

It has been shown that equilibrium charges and charge flux from electromagnetic radiations account quantitatively for several intermolecular electronic effects including induction and hyperconjugation [31, 32]. The interaction occurs with the releasing of electronic charge from σ_{C-H} to the C-C bond. In lead tartrate dehydrate, the most evident effect of this interaction is that the C-C bond decreases in length from its normal value and increases in strength [33–36], but effect of hyperconjugation can also be on C-H bonds. Electromagnetic radiation intensities have been directly correlated to spectral patterns. The asymmetric C-H stretching mode of tartrate ion is expected in the region around 2943 cm^{-1} . The O-H-O, intermolecular O-H bonding of the hydroxyl group with carbonyl group, causes the lowering of the O-H stretching mode. The calculated results help revealing for the first time that the synthesized molecule has microscopic nonlinear optical behavior with nonzero hyperpolarizability values. The electron donor group -OH and -CH and acceptor group -C=O play important role in the magnitude of second order polarizability. In lead iodide dihydrate sample, the analysis shows that the limited number of vibration peaks indicates the absence of second order harmonic generations while the hydroxyl stretching and bending bands can be identified by their broadness and strength of the band which depends on the extend of hydrogen bond [37–40]. Hydroxyl stretching vibrations are generally observed in the region around 3500 cm^{-1} . The hydroxyl stretching bands split into different bands that correspond to O-H and O-D. Interaction of lone pairs of oxygen (electron donor) with the O-H antibonding orbital leads to an increase of electron populations in this orbital, followed by a weakening of the O-H bond, which is accompanied by a lowering of the O-H stretching wavenumber. This explains the formation of the strong intermolecular hydrogen bonding between O-H group and lone pair of O in the molecule. Hydrogen bonding interaction leads to an increase in electron density of lead iodide crystals [41, 42]. It is evident that the electron density in O-H antibonding orbitals was significantly increased by the strong hydrogen bond between hydroxyl group (O-H) and lone pair of oxygen in the molecule providing unambiguous evidence about the weakening of the bond, its elongation, and shifts of the hydroxyl stretching frequency. Low wave number vibrations of hydrogen bonds indicate the attractive interaction between the hydrogen donor group and the acceptor metal group [43]. The low wave number degrees of freedom such as liberation as well as interaction induced give rise to additional absorption and Raman bands that frequently overlap with the bands of the hydrogen bond modes. The band in Raman at 96 cm^{-1} has been attributed to the translational motion of the hydrogen-bonded molecules including some bending component. The lattice vibrations of rotating type are generally stronger in intensity than the translatory type [27]. The lattice modes

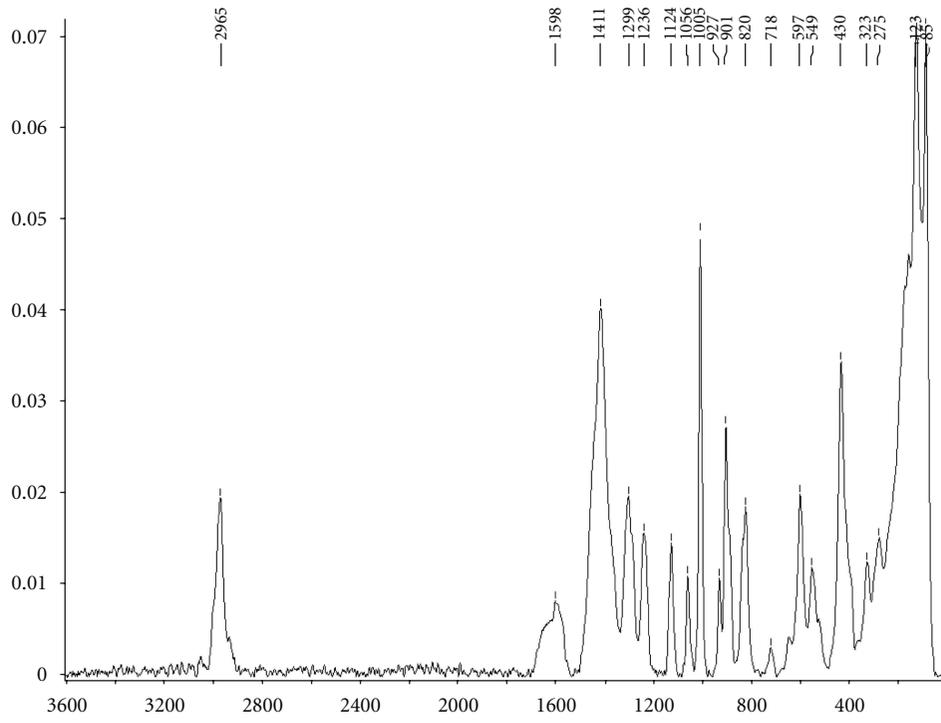


FIGURE 3: FT-Raman spectrum of pure lead tartrate crystal

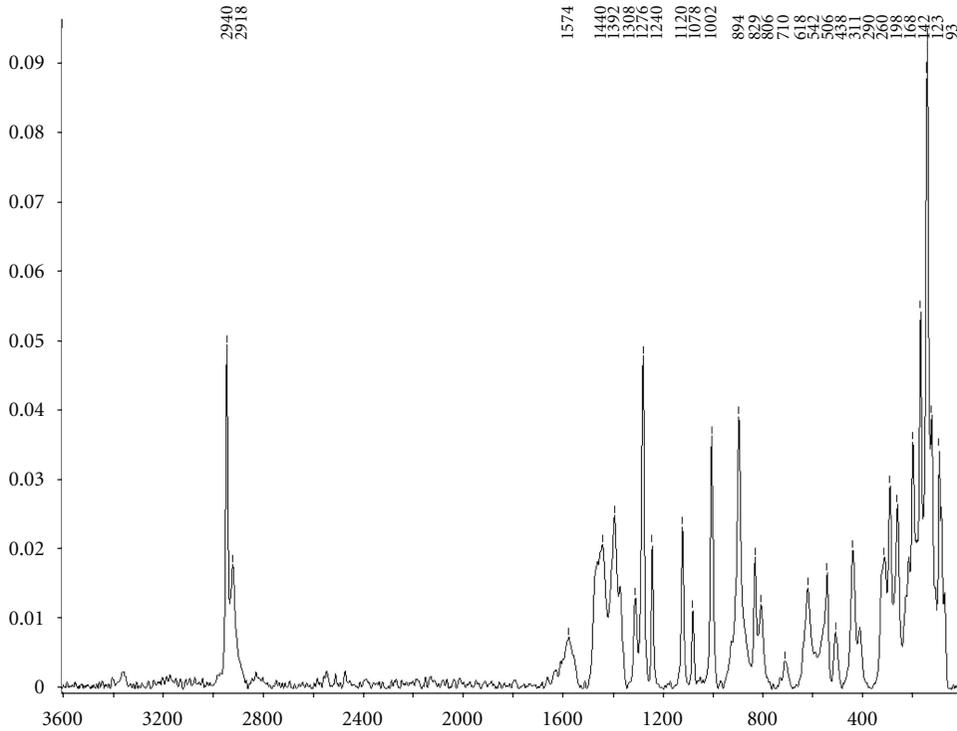


FIGURE 4: FT-Raman spectrum of doped lead tartrate crystal.

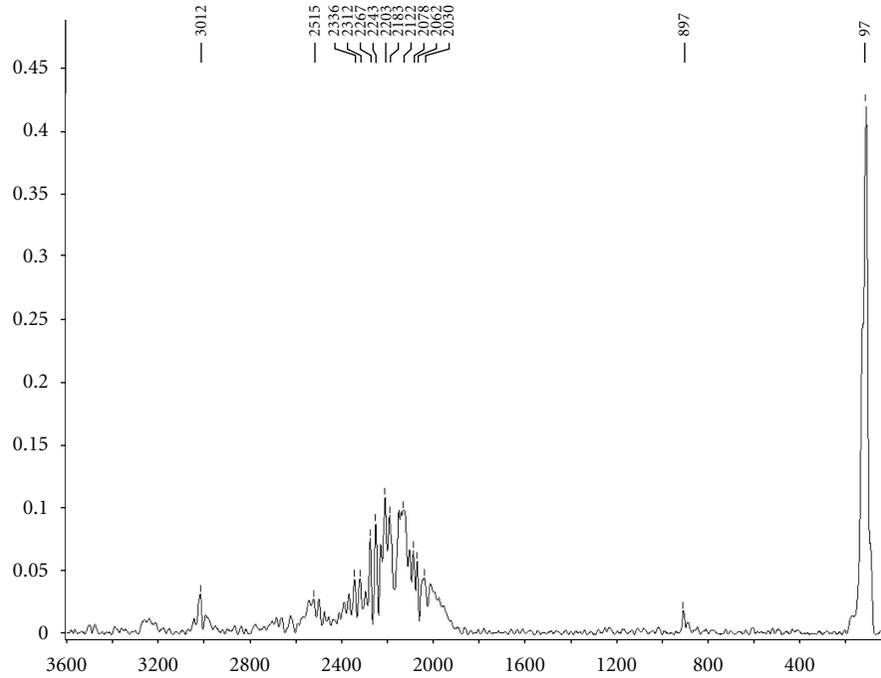


FIGURE 5: Fourier Transform Raman Spectrum of Pure Lead iodide crystal.

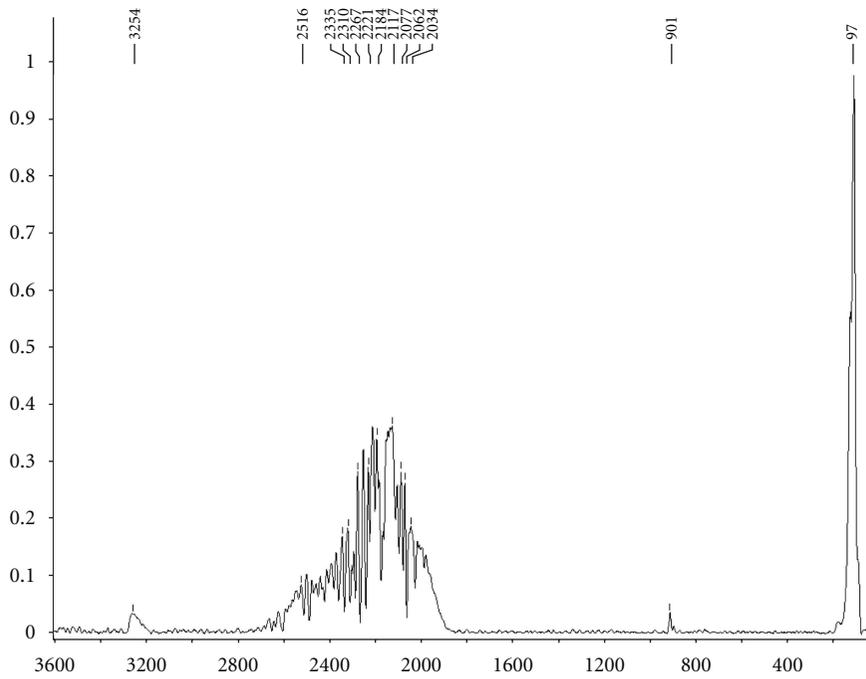


FIGURE 6: Fourier Transform Raman Spectrum of doped Lead iodide crystal.

are very intense in Raman. The calculations results also reveal that the synthesized molecule might have NLO behavior with nonzero polarization values. $(C_4H_4O_6)^{2-}$ is a tartrate ion [36–39], whereas in $PbI_2 \cdot 2H_2O$, I-Pb-I-Pb-I is the structure of lead iodide crystals forming a vandervals bond between

iodine atom. The analysis of bands obtained in Raman spectrum of lead tartrate and lead iodide crystals grown in pure and doped is shown in Table 1. In the stretching region, the tartrate ions and iodide give only limited resonating peaks, whereas in the region of nonlinearity the lead tartrate

gives large number of sharp peaks of the carbonyl, C–H, O–H all are in a state of tension and producing the peaks due to rocking torsion, in-plane, and out-of-plane bending of the functional group and the H–O–H group associated with the crystal. The bands at 500–548 cm^{-1} in the Raman spectrum have been identified as the O–H torsion mode. Hence, the band position of the O–H torsional mode may serve as a sensitive measure of the strength of the interaction between the O–H group and the lone pair electron of neighboring oxygen atom. The attractive interaction between the hydrogen donor group and the acceptor metal group leads to the occurrence of new vibrational degrees of freedom, the so-called hydrogen bond modes are connected with elongations, the relative distance between the metal and the associate ions and the relative orientations of the hydrogen bonded groups. Weak attractive interaction along the hydrogen bond, hydrogen bond mode occurs at low wave numbers in the range between 50 and 300 cm^{-1} . The bands at 57.44 cm^{-1} of lead tartrate have been attributed to the translational motion of the hydrogen-bonded molecules including some bending component. The lattice vibrations of rotatory type are generally stronger in intensity than the translator type. In lead iodide spectrum, the metal deformation bands occur at 96.88 cm^{-1} cause the lowering of the O–H stretching mode. In hydrogen-bonded inorganic systems, combination of bending modes with the internal rotation mode indicates that the ion is not rotating freely in the crystalline lattice. Crystal materials are widely used in many electro-optics fields, growing technologies and preparing technologies for nonlinear optical crystals. The high stability of PbI_2 verified by Raman spectra analysis. The results allow us to understand, at least partially, lead iodide crystal can yield noncentrosymmetrical by optical methods. Multiple bands present in the stretching region of water in the Raman spectrum with weak intensity in the region 2515–2003 cm^{-1} indicate the presence of hydrogen bonds of various strengths. On deuteration, the stretching modes of water molecules are shifted towards the low wave number region. Hydrogen bonding is an important interaction determining the structure and functionality of numerous molecular systems in nature Fermi resonance with the overtones of the $\delta(\text{OH})$ and $\nu(\text{OH})$ modes split into different bands near 2115–200 cm^{-1} . Stretching modes appear below 300 cm^{-1} C=O–H, the splitting of the carbonyl mode may be attributed to intermolecular association based on C=O...H type hydrogen bonding in the molecule and the structural and functional asymmetry in the carbonyl groups as shown in Figures 3 and 4. When a carbonyl group is participating in hydrogen bond and resonance can occur which puts a partial negative charge on the oxygen atom accepting the hydrogen bond and positive charge on the atom donating the hydrogen, the partial transfer of allegiances of the proton enhances resonance and lowers the CO stretching wave numbers. These mechanisms may be playing an important role in the biological activity. Raman spectrum can be used not only to obtain standard information, but also to evaluate the vibrational contribution (polarizability) to molecular hyperpolarization.

4. Conclusion

For tartrate group it is significant to consider a harmonic coupling for the low wave number modes, Fermi resonances with finger print vibrations (O–H bending and C=O stretch), and excitonic coupling between OH stretching modes, also known as Davydov coupling [43]. It is considered that stretching vibrations of the proton in the hydrogen bonded O–H–O are harmonically coupled to the hydrogen bond stretching vibrations. The splitting and lowering of the carbonyl stretching vibrational modes of tartrate indicate intermolecular association based on C=O–H type hydrogen bonding in the molecule. Raman spectrum corresponds to wave number 97 cm^{-1} is assigned to metal legands as shown in Figures 5 and 6. And wave number 1286 cm^{-1} is assigned to C–O stretching mode coupled with C–H in-plane bending mode of lead tartrate. Metal organic group of crystals thus belongs to second-order nonlinearity and metal inorganic group crystals correspond to third-order nonlinear crystals. Our results compared the motion of lead ions and the motion of functional groups in both the compounds using Raman spectra.

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