Journal of Molecular Structure 1143 (2017) 245–250

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Effect of VO^{2+} ions on the EPR and optical absorption investigations of lithium sulphate monohydrate single crystals for non linear optical applications

K. Juliet sheela [a], S. Radha Krishnan [b], V.M. Shanmugam [b], P. Subramanian [a,*]

[a] Department of Physics, Gandhigram Rural Institute-Deemed University, Gandhigram, Dindigul 624302, Tamilnadu, India
[b] CSIR-Central Electrochemical Research Institute, Karaikudi 63006, Tamilnadu, India

ARTICLE INFO

Article history:
Received 25 February 2017
Received in revised form
16 April 2017
Accepted 20 April 2017

Keywords:
Magnetic material
Crystal growth
Defects
Crystal fields
Electron paramagnetic resonance (EPR)

ABSTRACT

Electron paramagnetic resonance (EPR) and optical absorption studies of VO^{2+} ions in Lithium Sulphate Monohydrate (LSMH) single crystal are carried out at room temperature. Single crystal rotations in each of the three mutually orthogonal crystalline planes, ac, ab, cb indicate three different vanadyl complexes. Three VO^{2+} ions of EPR spectra indicate among them, that two of them have (the intense two) entered the lattice substitutionally and the third one occupies the interstitial position. From the angular variation, the spin Hamiltonian parameters are evaluated. From the optical absorption spectrum containing four selected bands and EPR data, various bonding parameters are determined and the nature of bonding in the crystal is discussed. Also Second Harmonic Generation (SHG) studies are carried out to confirm the Non Linear Optical (NLO) properties of the given material.

1. Introduction

EPR studies have been usually carried out by doping paramagnetic ions into diamagnetic hosts [1]. EPR spectroscopy is widely used to study metal complexes having at least one unpaired electron on the metal ion incorporated into the crystal lattice. EPR studies provide detailed information about the magnetic properties of transition metal ions. A detailed description of the ground state and nature of the crystalline electric field produced by the ligands surrounding the metal ion are supposed to be made quite accurately by EPR. The optical absorption results in conjunction with EPR results enable to calculate the molecular orbital coefficients, ground state energy level and types of bonding of impurity ion with the ligands. The EPR spectra of the VO^{2+} ion have revealed some interesting features about defect properties [2,3], host lattice effects, structural changes and orientation properties of the host lattice. Since the EPR spectrum is very sensitive to the crystalline environment, extensive EPR studies on VO^{2+} ions in a variety of lattices have been reported [4–7].

Recently a number of non centro-symmetric materials such as piezoelectric, pyroelectric and ferroelectric materials are utilized due to their potential applications like pyroelectric infrared detectors, fire detectors, dynamism of human sensors, pyroelectric nuclear fusion for neutron generation, microphones and lighters etc. NLO materials have gained importance due to their pertinent properties such as high laser damage threshold, wide transparency range and high nonlinear coefficient [8–11]. In the recent years, there has been extensive investigation in the growth of NLO materials because of their wide usage of optoelectronics and photonic applications [12,13]. NLO materials find a variety of applications to perform functions like frequency conversion, light modulation, optical memory storage, and optical switching [14]. Furthermore, LSMH crystal exhibits remarkable piezoelectric and electro optic properties [15]. Recently $Li_2So_4H_2O$ was classified as promising material for Raman laser frequency converters.

Generally, the transition metals have certain properties such as partly filled d-shell either as elements or compounds, good conductors of heat and electricity, high melting and boiling points. Also, they have several stable oxidation states, can be used as catalysts and many of them are paramagnetic (have unpaired electrons) in nature. Therefore using transition elements as a dopant, play a key role in improving the optical quality of the doped crystals. The presence of dopants enhance the optical properties [16] of

* Corresponding author.
E-mail address: psubramaniangri@gmail.com (P. Subramanian).

http://dx.doi.org/10.1016/j.molstruc.2017.04.082
0022-2860/

the VO^{2+} doped LSMH crystals and thus considered as a potential NLO candidates of the fabrication of electro-optic, NLO and opto-electronic devices. In general, these properties are sensitively dependent upon the local structures around the impurity ions in the host. Vanadyl ion (VO^{2+}) is the most stable cation among a few molecular paramagnetic transition metal ions, which is used extensively as an impurity probe for EPR studies.

EPR investigation on Cu^{2+} doped LSMH single crystal [17] has been carried out by the same authors and the promising results like crystal field symmetry, location and ground state energy of the impurity ion was reported for single site as an interstitial site. In the present case of VO^{2+} doped LSMH single crystal along with above said parameters, the molecular orbital coefficients and types of bonding of impurity with the ligands and the SHG studies have also been reported for three observed sites (2 substitutional sites and one interstitial).

2. Experimental

2.1. Sample preparation

Analytical reagent (AR) grade of LSMH was dissolved in double distilled water and saturated solution was obtained. 1% by molecular weight of vanadium (II) sulphate pentahydrate was added to the saturated solution as an impurity. The crystals were grown by slow evaporation technique at room temperature in two weeks period. Repeated recrystallization was carried out in order to get good quality of size $5 \times 3 \times 2$ mm^3 LSMH single crystal.

2.2. LSHM crystal structure

LSMH ($Li_2SO_4H_2O$) single crystals are monoclinic with P_{2_1} point group. Redetermination of the crystal structure of LSMH was carried out [18]. The dimensions of unit cell are a = 5.43 Å, b = 4.84 Å, c = 8.14 Å, $\alpha = \gamma = 90°$, $\beta = 107°$ with two molecules per unit cell. The sulfur atom is surrounded by four oxygen atoms tetrahedrally. Similarly Li_1 and Li_2 are surrounded by four oxygen atoms tetrahedrally.

2.3. Characterization techniques

The EPR measurements were performed on Bruker EMX plus spectrometer operating at X-band microwave frequency of 9.85 GHZ with 100 KHZ field modulation. The angular variation spectra were recorded along the three mutually perpendicular directions to the crystal axes for every 10° interval. The optical absorption spectrum was recorded at Perkin Elmer lamda-35 UV–Vis–NIR spectrometer in the wavelength range of 200–1200 nm. The SHG measurement of the VO^{2+} doped LSMH single crystals was carried out employing Kurtz perry powder technique with the pulse width of 9 ns and repetition rate of 10 Hz. The EPR spectral data in the three planes have been analyzed using the package program 'Origin-8'. The matrices are diagonalized by 'Matlab 2012 a' computer software program.

3. Results and discussion

3.1. EPR spectral analysis

The chosen LSMH crystal was mounted on the crystal mount and rotated about mutually perpendicular morphological axes in the EPR cavity. Vanadyl ion (V^{4+}) has the electronic configuration [Ar] $3d^1$, which thereby leads to paramagnetism in VO^{2+}. The ^{51}V nucleus (99.8%) abundant has a nuclear spin of I = 7/2 and a large magnetic moment. Generally, an eight line pattern of EPR spectrum is expected for a vanadyl impurity when the applied magnetic field

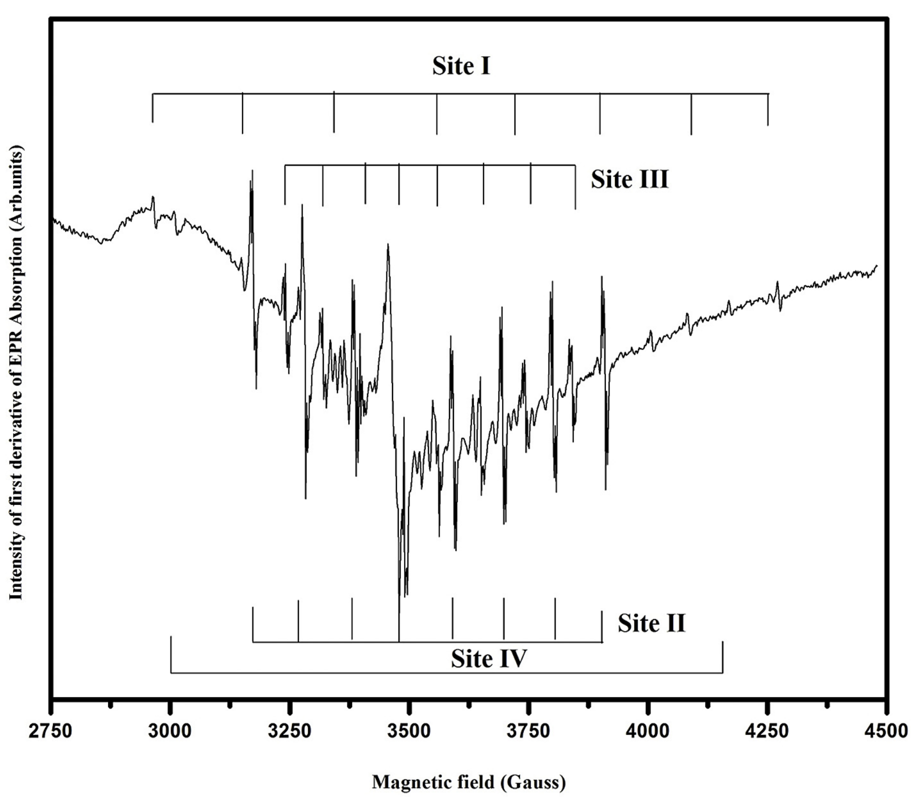

Fig. 1. First derivative of EPR absorption spectrum of VO^{2+} doped lithium sulphate monohydrate single crystal with magnetic field 170° away from c axis.