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EPR Analysis of Cu^{2+} ion Doped Potassium borodicitrate Single Crystal

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Abstract

In our present investigation single crystals of Potassium borodicitrate (KBDC) (for a fixed content-host lattice) with Cu^{2+}, a guest species, as a dopant (at four 0.2, 0.5, 1 and 2 g) in weight ratio have been synthesized at room temperature by using slow evaporation method. These as-synthesized 4 crystals have been subjected to Electron Paramagnetic Resonance (EPR) studies. The EPR spectrum shows that 0.5 g dopant KBDC give a 4 equidistant hyperfine lines with the perfect symmetry confirms that the localization of Cu^{2+}, a paramagnetic impurity, within it reveals that the maximum absorption of EPR signals happens at 0.5 g Cu^{2+} than any other concentrations with reference to 20° in horizontal plane than the normal and vertical recording in the same angular projection. The Spin Hamiltonian calculations are used to obtain spectroscopic field splitting factor g-tensor values, g_{xx} = 2.0421, g_{yy} = 2.1962, g_{zz} = 2.2827 and hyperfine splitting factor A-tensor values A_{xx} = 150, A_{yy} = 112 and A_{zz} = 134. The K–O bond length associated with directional cosines of g_{zz} tensor reveal that the Cu^{2+} is located interstitially. This optimized single crystal has furtherance been subjected to Single cystal X-ray diffraction (SXRD), Fourier transform infrared Spectrascopy (FTIR).

Scanning electron microscope (SEM) Energy dispersive X-ray analysis (EDAX) and compared with pure KBDC single crystal. The XRD unit cell crystalline parameter variations reveal that there is doping effect of Cu^{2+} into the host lattice brings forth structural coordination of Cu^{2+} with KBDC. The FTIR confirms that complexation of host and guest through molecular interactions in the finger print region. The EDAX mapping shows Cu^{2+} presence in the crystal.

Keywords: Electron Paramagnetic Resonance (EPR), Potassium borodicitrate, Spin Hamiltonian parameters

Introduction

Magnetic resonance technique is a suitable method for investigating the atomic behaviour of crystals such as symmetry, the interstitial defects, absorption of radiation and impurity effects in crystals and so on. The inclusion or emission of electromagnetic rays in the microwave range expressed as 'magnetic resonance', which provides information about the paramagnetic defect center present in investigated crystal. Based on the working region in the electromagnetic spectrum the magnetic resonance such as Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) is in microwave region and Nuclear Magnetic Resonance (NMR) is in radio wave region. EPR is an only spectroscopic practice which is capable of finding out the presence of unpaired electrons explicitly in any species.

EPR studies generally deals with paramagnetic impurities doped with either diamagnetic or paramagnetic hosts. The local environmental symmetry of the analyzing complexes in the host lattices can be determined with the help of transition metal ions as a probe. Since the Cu^{2+} has $3d^9$ configurations, which represents a simple 1 magnetic hole system [1-8], it enters the lattice replacing the divalent cation either substitutionally or interstitially.

The pure crystals will not absorb any EPR signal because of the paired electronic configuration in the host lattice, but it absorbs the same by doping the some paramagnetic impurity as it contains unpaired electrons. In the present investigation Cu^{2+} doping accomplishes the absorption phenomena for the as-synthesized single crystal. This absorption of EPR signal by the crystalline domain of the single crystal distinctly explores the local field symmetry through the coordination geometry of host guest in turn deals to interpret the atomic properties such as, site symmetry of the doped metal ion in the lattice, energy levels in the ground state, bonding parameters, phase transition, spin relaxation time, etc.

Basically, all materials exhibit non linear optical phenomena (NLO), this includes all forms of matter. However, from the device point of view, non linear optical materials in the solid format are of great use.

Albeit the organic non linear optical crystal (NLO) exhibit poor optical transparency high nonlinear coefficient and structural diversity, they have good efficiency. On the other hand, inorganic NLO crystals exhibit high optical transmission but poor efficiency. The merits of organic NLO crystal are combined with merit of inorganic NLO crystals and as a result a new form of organic-inorganic NLO crystal is developed. Generally the slow evaporation solution growth technique is employed as a facile method for synthesizing inorganic-organic single crystal otherwise referred as semi organic single crystal. Some of them are potassium boro-succinate, potassium boro-oxalate, etc., have been studied. The semi organic crystals have very good NLO properties with good thermal and high mechanical stability [9,10].

The pristine potassium borodicitrate (KBDC) single crystal have been synthesized by Zviedre *et. al* and reported its detailed crystal structure [9,10]. However, the EPR study is yet to be conducted on KBDC single crystal particularly with reference to Cu^{2+} paramagnetic impurity. So, the present investigation an attempt has made to explore the EPR studies on KBDC-Cu^{2+} single crystal at ambient temperature by using slow evaporation practice for the different variants of Cu^{2+}. The structural and morphological features of the Cu^{2+} doped KBDC crystal investigated and the results are discussed.

Materials and methods

Synthesize of KBDC-Cu^{2+} crystal

Slow evaporation technique has been used to synthesize single crystals of KBDC-Cu^{2+} by varying the Cu^{2+} at 4 different weight ratios at room temperature. To grow single crystals, the pre-cursors potassium hydroxide, boric acid, citric acid is taken in 1:1:2 proportion with Cu^{2+} as dopant which is immersed in highly purified water and mixed uninterruptedly for 3 h for getting a standard solution. The as obtained saturated solution is filtered by using Whatsman filter paper (180 µm). The filtered solution collected into a 2 inch petri dish and it is sealed tightly using aluminum foil with small holes in it to control the rate of evaporation naturally and it is kept at dust free environment for natural evaporation. Eventually the transparent single crystals of Cu^{2+} doped KBDC are obtained after 15 days. The same procedure is repeated for different weight ratios of the dopant. To improve the quality of the crystal it is taken to the successive recrystallization process. **Figure 1** shows the collected pure and doped single crystal of the size of 4×6×5 mm^3 and 4×6×2 mm^3, respectively.

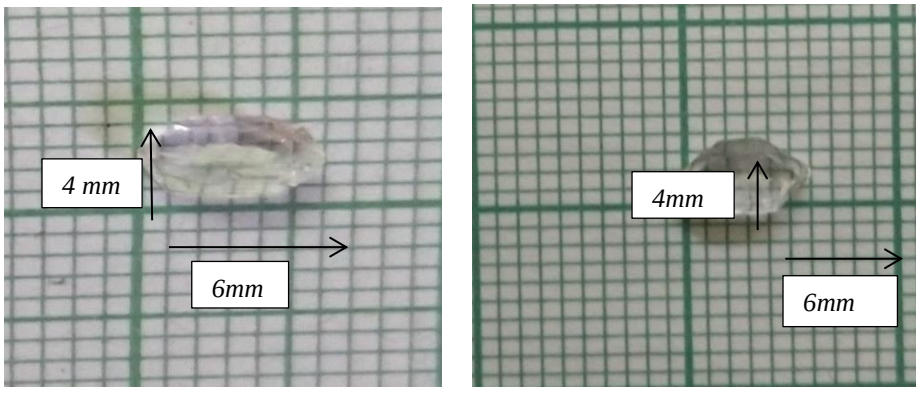


Figure 1 Photograph of pure and Cu^{2+} doped KBDC single crystal.

Results and discussion

SXRD studies

A SXRD study is one of the non destructive testing (NDT) methods which provide detailed information about the lattice parameters of the as synthesized crystals. SXRD analysis has been recorded at room temperature by using Bruker AXES Kappa APEX II single crystal X-Ray diffractometer with MoKα (λ = 0.710 Å) radiation for both pure and Cu^{2+} doped KBDC single crystals. It is observed that the pure KBDC and doped KBDC crystal structures are orthorhombic with space group P_{bca}, Lattice constant of the pure KBDC and Cu^{2+} doped KBDC observed are almost found to be the same as shown in **Table 1**.

Table 1 Comparison of lattice constant.

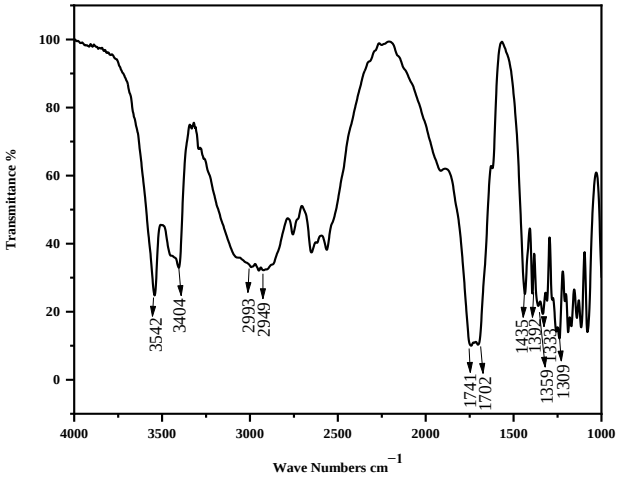
Lattice constant	Single crystal XRD	
	Pure KBDC	**Cu^{2+}-KBDC**
a (Å)	10.110	10.127
b (Å)	11.170	11.159
c (Å)	33.105	33.126
α	90°	90°
β	90°	90°
γ	90°	90°
Volume ($Å^3$)	3750.5	3775.4
Crystal system	orthorhombic	orthorhombic
Space group	P_{bca}	P_{bca}

FTIR analysis

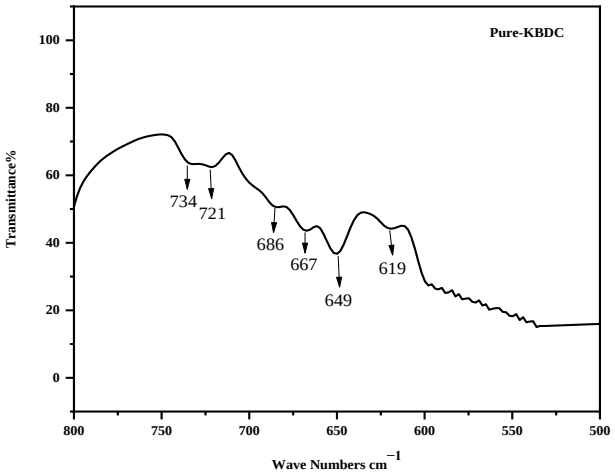
FTIR analysis deals with the molecular composition and structure of the sample used by measuring the sample's optical density at various wavelengths. The transmittance peaks of infrared spectra are also called absorbance bands, which correspond with the various vibrations of the sample's atoms when it's exposed to the infrared region of the electromagnetic radiation. These bands are grouped as functional groups frequencies such as CH_2, OH and C=O can be seen above 1500 cm^{-1} in the infrared spectrum and fingerprint frequencies, deals with highly characteristic of the molecule as a whole; they tell what is going on within the molecule, they can be seen below 1500 cm^{-1} in the infrared spectrum however, some functional groups will absorb in this region as well. As a result, compare to the presence of a band in this region, the absence of a band is often more indicative in the spectrum and is less reliable for identification.

The infrared spectrum of the pure KBDC single crystal is noted between the frequency ranges from 400 - 4000 cm^{-1}. The C–H stretching vibrations (sym/asym) for KBDC occur at 2993 and 2949 cm^{-1}. The O–H (sym/asym) stretching vibration at 3542 and 3404 cm^{-1} confirms the presence of hydrate (H_2O). The vibrational band at 1702 cm^{-1} refers to C=C and 1741 cm^{-1} corresponds to C=O. The absorbance band at 1435, 1392 and 1359 cm^{-1} correspond to in plane/out of plane bending vibration associated to C–O and the absorbance band found at 1333 and 1309 cm^{-1} confirms the methylene group presence. The absorbance band at 735 and 721 cm^{-1} are assigned to B–O bending vibration. The peaks at 620, 650, 668 and 686 cm^{-1} correspond to O–H out of plane bending. **Figure 2**(**a**), show FTIR analysis for pure and Cu^{2+} doped KBDC presence of functional group in the higher wavenumber region between 1000 - 4000 cm^{-1} [11,12].

After doping the paramagnetic impurity of Cu^{2+}, the FTIR spectrum recorded and its effect is referred with respect to pure KBDC spectrum. It is observed very obviously that the participation of Cu^{2+} is well seen with the appearance of new absorbance band at 596 cm^{-1} corresponds to Cu–O [13] in the fingerprint region between 400 - 1000 cm^{-1} **Figures 2**(**b**) and **2**(**c**).



(a)



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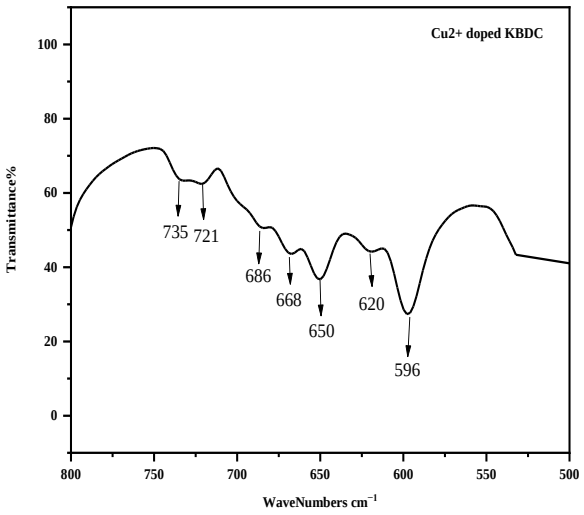


(c)

Figure 2 FTIR analysis for pure and Cu^{2+} doped KBDC with presence of functional group elements in the higher wavenumber region between 1000 - 4000 cm^{-1} (a), comparing the FTIR spectra of pure KBDC (b) and Cu^{2+} doped KBDC single crystal (c). It is noted that the presence of copper at 596 cm^{-1} in the finger print region between 500 - 800 cm^{-1}.

EPR spectral analysis and calculation of EPR parameters

EPR spectra are recorded by using Bruker EMX plus spectrometer working at X-band microwave frequency (9.8 GHz) and employing a 100 kHz magnetic field modulation at ambient temperature. The analysis of EPR is recorded by rotating the quartz rod (where the single crystal is placed) in 3 mutually perpendicular directions in 10° steps in each plane from 0° to 180° for all the planes as bc, ca and ab respectively.

The paramagnetic impurity Cu^{2+} ion, has unpaired electrons at the outermost orbital in $3d^9$ electronic configuration. These unpaired electrons whoseelectron spin is S = ½ and the nuclear spin is I = 3/2, which are responsible for the presence of 4 hyperfine lines with allowable transitions (ΔMs = 0, ΔMI = ±1). According to energy level diagram, the Cu^{2+} ion should have 4 hyperfine lines [14]. The presence of single Cu^{2+}ion in the lattice is shown in **Figure 3**.

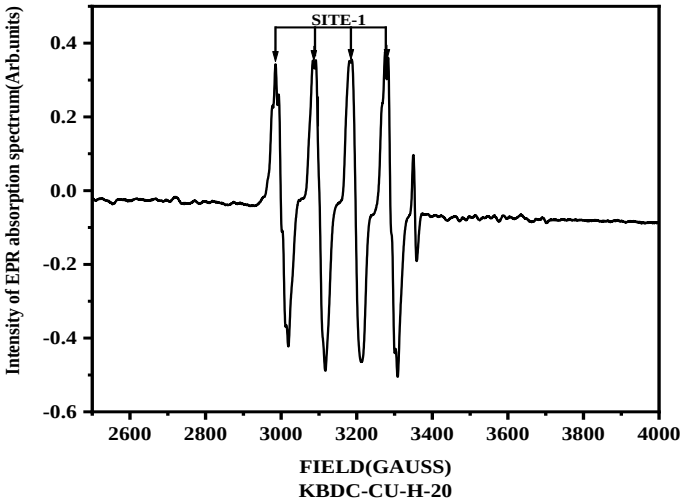


Figure 3 EPR spectrum of Cu^{2+} doped KBDC single crystal with magnetic field at an angle 20° from c axis in the cb plane at ambient temperature.

Angular variation calculations using EPR spectra

Using the hyperfine lines in the graph in all the orthogonal planes ab, bc and ca, the experimental external magnetic field values are observed. Using the maximum and minimum of these observed values, theoretical magnetic field (H) and theoretical spectroscopic splitting factor (g) are calculated using the following equation with MATLAB.

$$g^2(\theta) = \alpha + \beta \operatorname{Cos} 2\theta + \gamma \operatorname{Sin} 2\theta \quad (1)$$

Where $\alpha = g^2_{maxi} + g^2_{mini}/2$
$\beta = (g^2_{maxi} - g^2_{mini}) \operatorname{Cos} 2\theta_{maxi}/2$
$\gamma = (g^2_{maxi} - g^2_{mini}) \operatorname{Sin} 2\theta_{maxi}/2$

where 'g' is a tensor, its value is 2.0023 for free electron, which deals with the magnetic moment of the paramagnetic ion. The maximum and minimum g tensor values are noted as g_{maxi} and g_{mini} and θ is angle formed due to rotation of the crystal in the orthogonal planes bc, ca and ab from 0° to 180°.

The angular variations associated in these planes as shown in **Figure 4**. These derived parameters obtained from the experimental and analytical H values (a straight line representing analytical points and the solid circle representing experimental points) both revealed the local symmetry of the crystal as orthorhombicin accordance with Jorgensen crystal field theory [15,16] i.e., according to Jorgensen crystal field theory, from the observed g_{xx}, g_{yy} and g_{zz} values, the site location symmetry surrounding the Cu^{2+} ion in the host crystal lattice can be determined. When g_{xx}, g_{yy} and g_{zz} are equal ($g_{xx} = g_{yy} = g_{zz}$) then it corresponds to cubic symmetry, if g_{xx} is not equal to g_{yy} and g_{zz} ($g_{xx} \neq g_{yy} = g_{zz}$) then it corresponds to axial symmetry and if all g_{xx}, g_{yy} and g_{zz} ($g_{xx} \neq g_{yy} \neq g_{zz}$) are not equal then it corresponds to orthorhombic

symmetry. Since (in our present case) the characteristics of Cu^{2+} ion show the g tensor corresponds to $g_{xx} \neq g_{yy} \neq g_{zz}$ so as synthesized KBDC-Cu^{2+} is orthorhombic symmetry in nature [17].

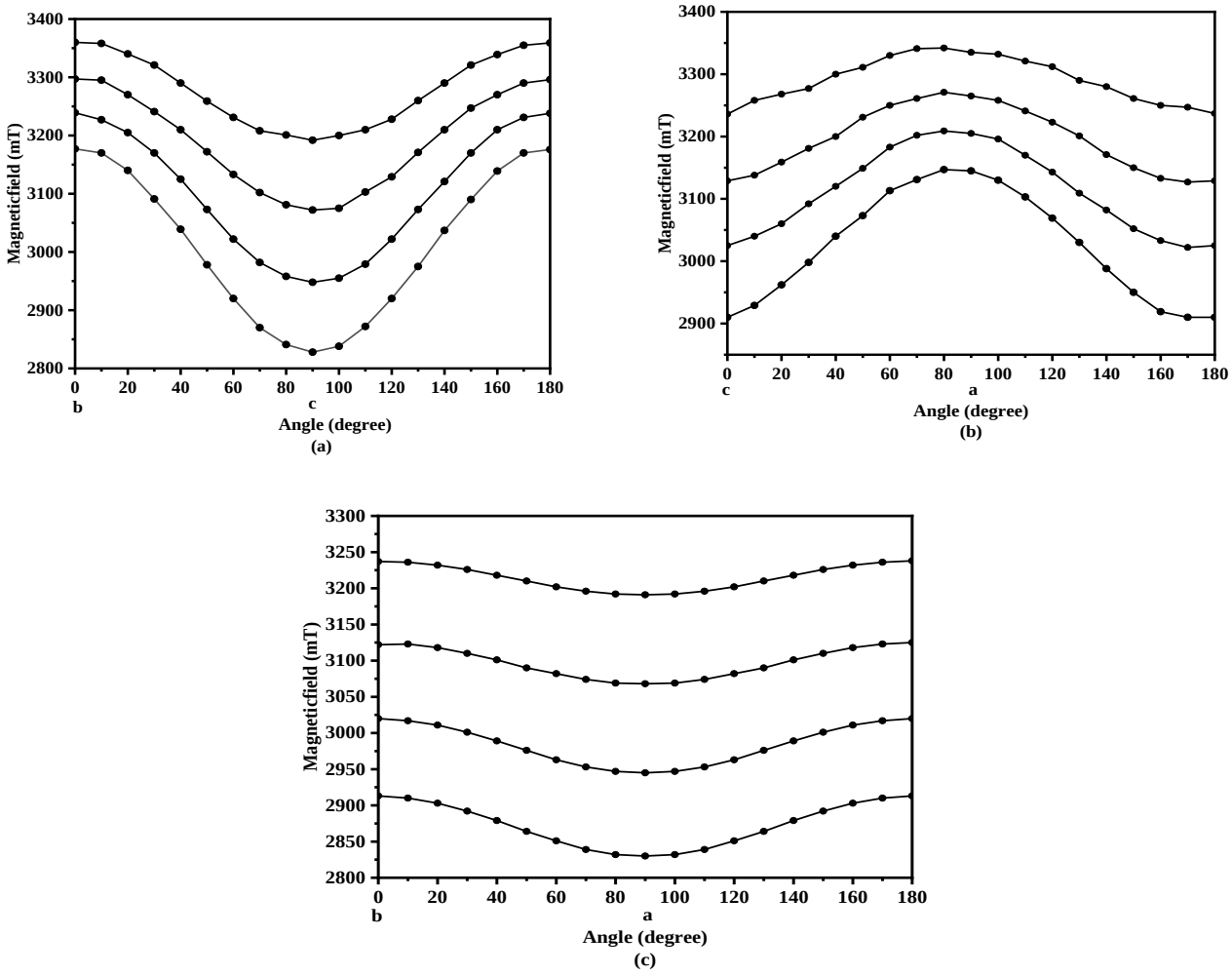


Figure 4 Angular variation plot of Cu^{2+} doped KBDC spectra in 3 mutually orthogonal planes.

The angular projections or orientations of as-synthesized crystal Cu^{2+}-KBDC are expressed in terms of the directional cosines (l, m and n). These directional cosines are obtained using Schonland's procedure [18] and thereafter the corresponding spin Hamiltonian $\mathcal{H}$ are calculated (**Table 3**) using the following equation.

$$\mathcal{H} = \beta(g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z) + A_{xx}I_xS_x + A_{yy}I_yS_y + A_{zz}I_zS_z \quad (2)$$

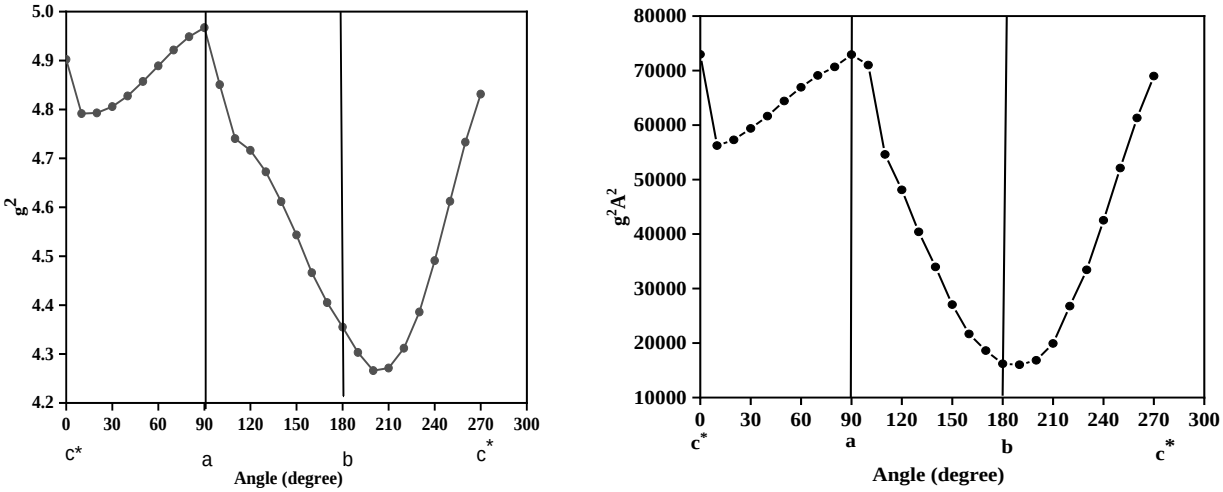
Where the electron spin vector is (S) and the hyperfine separation is (A).

Table 3 Estimation of spin Hamiltonian parameters ($\mathcal{H}$) for Cu^{2+} doped KBDC.

Site	g-tensor	Directional cosines			A tensor	Directional cosines		
		l	m	n		l	m	n
I	g_{xx} = 2.0421	0.9551	–0.2868	0.0729	A_{xx} = 150	–0.9481	–0.2773	–0.1554
I	g_{yy} = 2.1962	0.2470	0.6368	–0.7303	A_{yy} = 112	–0.1198	0.7646	–0.6331
I	g_{zz} = 2.2827	–0.1630	0.7156	0.6792	A_{zz} = 134	–0.2944	0.5816	0.7582

Angular variation of g^2 and g^2A^2-confirmation of site location symmetry of Cu^{2+}-KBDC

Figures 5(**a**) and **5**(**b**) show the angular variation coincidence of g^2 with g^2 A^2 in the orthogonal planes ab, ca and bc, which confirms that as-syntheized single crystal shows orthorhombic symmetry [19].



(a) (b)

Figure 5 Angular variation plot of g^2 for orthogonal planes of Cu^{2+} doped KBDC single crystal (a) and Angular variation plot of g^2 A^2 for orthogonal planes of Cu^{2+} doped KBDC single crystal (b).

Impurity site location symmetry

The crystallographic data are used to find the impurity site location. The direction cosines of largest atom (K) bonding with different oxygen and water molecules in the KBDC system are given in **Table 4**. These values are supportive to confirm the location of the paramagnetic impurity.

Table 4 Direction cosines of Potassium with their nearby atoms in KBDC.

Bond	Bond length (A) (UNIT)	Direction cosines		
		l	m	n
K–O_1	2.985	–0.3832	0.3596	0.3212
K–O_2	2.638	0.2389	0.5089	0.3156
K–O^3	3.141	–0.0856	0.2538	0.3450
K–O_4	3.157	0.0359	0.4288	0.3495
K–O_9	2.625	–0.1998	0.1548	0.4334
K–O_{11}	3.028	–0.1236	0.3943	0.4010
K–H_2O II	2.846	0.3788	0.2359	0.3834

It is customary to relate the bond length K–O_x (x = 1, 2, 3, 4, 9, 11) of KBDC crystal direction cosines with principal g_{zz} tensor values and it is found that the compared values are not matching, reveal that the location of the paramagnetic impurity has entered the lattice in the interstitial location. From **Tables 3** and **4** the values of g_{zz} tensor orientation do not have good agreement with any of the bond directions of KBDC crystal system and this indicates the Cu^{2+} ion preferred to occupy the interstitial position rather than substitutional site. Generally if the atomic radii of the host ion (K) are larger then it will be replaced by the paramagnetic ion (Cu^{2+}) substitutionally. In the current study due to the presence of 2 chelate rings as a part α-hydroxyl and carboxyl group of 2 citrate ions, the boron atom with oxygen atom strongly coordinate with K ions. Therefore, the added impurity prefers interstitial location [20].

Calculations of energy level at ground state and molecular orbital analysis of Cu^{2+} ion

Ground state energy level

Evaluation of ground state energy level of Cu^{2+} in the host lattice can be determined by using the Rache parameter given in Eq. (3).

$$R = (g_{yy} - g_{xx})/(g_{zz} - g_{yy}) \quad (3)$$

The unpaired electron predominance is $d_{x^2-y^2}$ state if the value of R is lesser than one; the unpaired electron is $d_{3z^2-r^2}$ if the value R is greater than one. Hence the ratio of spectroscopic splitting factor indicates the Cu^{2+} ion is in $d_{3z^2-r^2}$ ground state [21].

Molecular orbital analysis of Cu^{2+}

The molecular orbital analysis of the impurity ion is also evaluated by using the following relations and is tabulated in **Table 5**. The parallel and perpendicular components of g and A tensor are ($g_\perp$, $g_\parallel$, $A_\perp$ and $A_\parallel$) calculated by using the following relation.

$$g_\perp = (g_{xx} + g_{yy})/2,\ g_\parallel = g_{zz}, \quad (4)$$

$$A_\perp = (A_{xx} + A_{yy})/2,\ A_\parallel = A_{zz}, \quad (5)$$

It is found that the properties of as-synthesized crystal vary with different crystallographic orientations and is said to be anisotropic. The parameter (g_{iso} and A_{iso}) is determined by using the following expressions.

$$g_{iso} = (2g_\perp + g_\parallel)/3 \quad (6)$$

$$A_{iso} = (2A_\perp + A_\parallel)/3 \quad (7)$$

The tetragonal distortion level can be estimated by the ratio of $\Delta g_\parallel/\Delta g_\perp$.

$$\Delta g_\parallel/\Delta g_\perp = (g_e - g_\parallel)/(g_e - g_\perp) \quad (8)$$

It is observed that the estimated ratio is greater than unity which implies that Cu^{2+} ion is more tetragonally distorted [22]. The dipolar hyperfine coupling constant (P), Fermi contact term (k) and the covalency nature (α^2) are also evaluated by using the expressions.

$$P = 7(A_\parallel - A_\perp)/6 \quad (9)$$

$$k = -(A_{iso}/P) - (g_e - g_{iso}) \quad (10)$$

$$\alpha^2 = A_\parallel/0.036 + (g_\parallel - 2.0023) + 3/7(g_\perp - 2.0023) + 0.04 \quad (11)$$

The delocalization of the d-electron can be found by using the dipolar term (P), which is 360×10^{-4} cm^{-1} for free ion. The d-electron delocalization is found to be 12.5 % and unpaired electron density on Cu^{2+} is 87.5 % and the remaining density is being shared onto the ligands. The bonding effects on the Cu^{2+} in the crystal lattice by using fermi contact term (k) is found to be 0.39 and it is consistent with the

3d transition metal ion is 0.36. The covalent nature of σ bonding α^2 is 0.6455 indicating that metal ligand bond of Cu^{2+}/KBDC is moderately covalent between ionic and covalent bond [23,24].

Table 5 Molecular bonding coefficients of g and A of Cu^{2+} ion in KBDC single crystal at ambient temperature.

Complex	$g_{\|\|}$	$g_{\perp}$	g_{iso}	$A_{\|\|}$	$A_{\perp}$	A_{iso}	$\frac{(ge-g\,\|\|)}{(ge-g\perp)}$	P	k	α^2
KBDC	2.0421	2.2395	2.1733	150	123	182	1.6779	315	0.399	0.6455

SEM and EDAX studies

The surface analysis (SEM) and elemental composition (EDX) of the as-synthesized crystal are recorded using the Hitachi S-3000 scanning electron microscope. The as-synthesized single crystal is sliced into few mm and its surface with various magnification positions is observed. **Figures 6**(**a**)-**6**(**e**) show various magnifications of the as grown crystal with layered structure i.e., at 50, 10 and 5 µm magnification respectively [25].

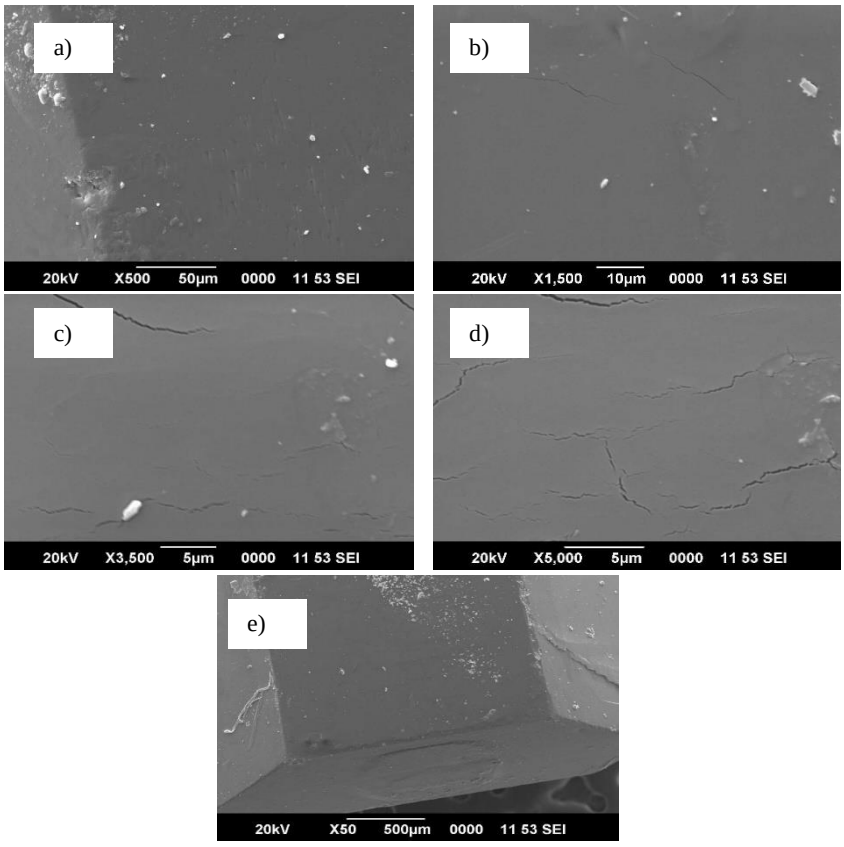
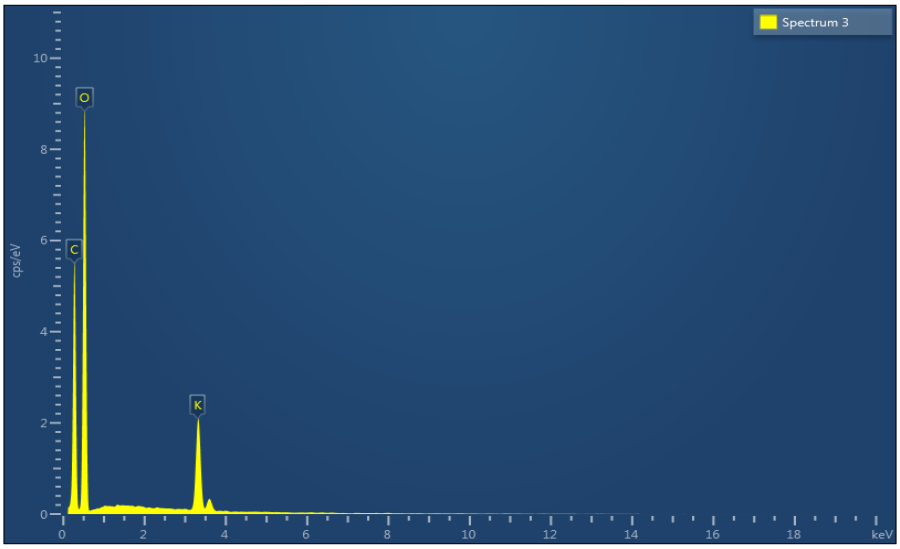


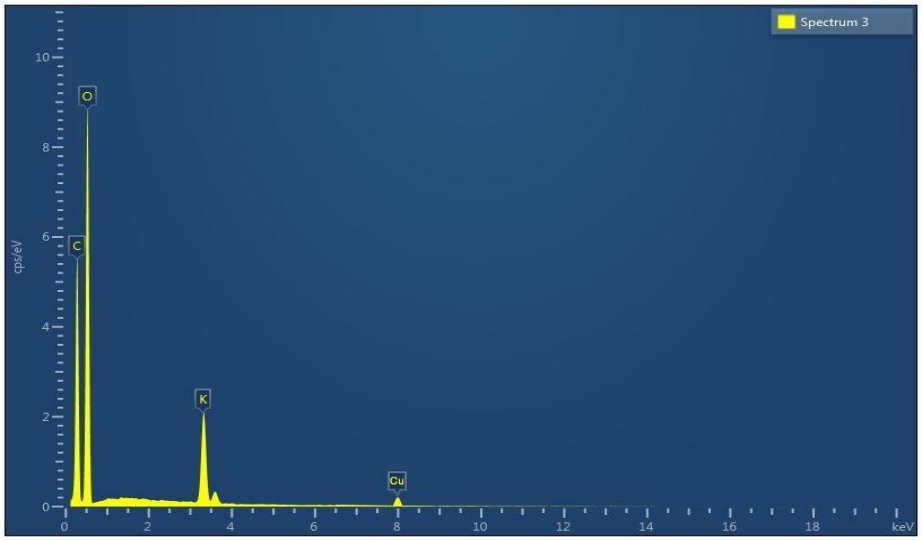
Figure 6 SEM images of grown KBDC-Cu^{2+} crystal.

Using EDX analysis a graph was plotted between the energy and absorption intensity for both pure and Cu^{2+} doped samples **Figures 7**(**a**) and **7**(**b**).

The element present in the sample and its weight percentage for both pure and Cu^{2+} doped KBDC are given in **Table 6** it is evident that the amount of Cu^{2+} has entered the crystal lattice of KBDC [26].



(a)



(b)

Figure 7 EDAX Spectrum of Pure KBDC single crystal (a) and EDAX Spectrum of Cu^{2+} doped KBDC single crystal (b).

Table 6 EDAX quantification of Pure and Cu^{2+} doped KBDC single crystal.

S. No.	Elements	Wt% (Pure)	Wt% (Doped)
1	C	37.25	37.25
2	O	57.34	57.34
3	K	5.41	4.91
4	Cu	-	0.50
	Total	100	100

Conclusions

The current study, single crystal of Cu^{2+} doped KBDC has been grown at room temperature. The paramagnetic ion Cu^{2+} has entered the interstitial location in the lattice. The as-synthesized single crystal is taken for orientation from 0° to 180° for all the planes as bc, ca respectively. Angular variation calculation of both Experimental and Theoretical revealing orthorhombic symmetry of the crystal and it obeying Jorgensen method. The evaluation of the principal g and A values of spin Hamiltonian reveals that the EPR spectra is fitted to orthorhombic crystal field symmetry. On comparing the directional cosines of g_{zz} tensor values do not have good agreement with any of the bond direction of KBDC crystal system and hence it is confirmed that the Cu^{2+} ion occupies the interstitial location lattice in the. On observing the principal g tensor values it shows that $g_{zz} > g_{yy} > g_{xx}$ and thus confirmed $d_{3z}{}^2{}_{-r}{}^2$ is the ground state for Cu^{2+} ion. The covalent bonding nature $\propto^2$ value indicates that it is moderate between ionic and covalent i.e., the bonding nature lies between the metal and the ligands. In addition to the EPR analysis, Single crystal XRD studies gives the lattice constant of pure and Cu^{2+} doped KBDC single crystal, FTIR gives the presence of functional group element present in the Cu^{2+} doped KBDC single crystal, surface morphology of Cu^{2+} doped KBDC single crystal are studied by SEM analysis and EDAX studies gives the percentage of absorption by the element present in Cu^{2+} ion doped KBDC single crystal respectively.

References

[1] S Radhakrishna and M Salagram. Orientational (EPR) study of vanadyl ion in potassium hydrogen oxalate lattice. *Solid State Commun*. 1983; **47**, 77-82.

[2] VK Jain. EPR of Mn^{2+} and VO^{2+} in $K_2C_2O_4{\cdot}H_2O$ single crystals. *Phys. Status Solidi B* 1980; **97**, 337-44.

[3] JA Wiel and JR Bolton. *Electron paramagnetic resonance*. Wiley, New York, 1994.

[4] B Natarajan, S Mithira, S Deepa and P SambasivaRao. EPR and optical investigation of VO(II) in $Zn(C_3H_3O_4)_2(H_2O)_2$ single crystals: An interstitial site. *J. Phys. Chem. Solids* 2007; **68**, 1995-2002.

[5] R Kripal and DK Singh. ESR and optical study of Cu^{2+}-doped *Bis*(l-asparaginato)zinc(II). *J. Phys. Chem. Solids* 2006; **67**, 2559-66.

[6] P Subramanian, SR Krishnan and VM Shanmugam. Elucidation of site symmetry, location, bond, ground state of Cu^{2+} ions in lithium sulphate monohydrate single crystal through EPR and optical studies. *J. Mol. Struct.* 2020; **1206**, 127586.

[7] KJ Sheela, SR Krishnan, VM Shanmugam and P Subramanian. Analysis of spin-Hamiltonian and molecular orbital coefficients of Cu^{2+} doped $C_8H_{11}KO_8$ single crystal through EPR technique. *J. Mol. Struct.* 2018; **1158**, 66-74.

[8] N Subbulakshmi, KJ Sheela and P Subramanian. Single crystal EPR studies of Cu^{2+} ion doped lithium potassium phthalate. *AIP Conf. Proc*. 2017; **1832**, 100009.

[9] II Zviedre, VS Fundamenskii, VV Krasnikov and GP Kolesnikova. *Akad Nauk Latv SSR Ser Khim.* 1982; **25**, 95-101.

[10] MK Dhatchaiyini, G Rajasekar and A Bhaskaran. *J. Mat. Sci.* 2019; **54**, 9362-71.

[11] J Coates. *Interpretation of infrared spectra: A practical approach*. *In*: Encyclopedia of analytical chemistry: Applications, theory and instrumentation. John Wiley & Sons Ltd., Chichester, 2006.

[12] D Peak, GW Luther III and DL Sparks. ATR-FTIR spectroscopic studies of boric acid adsorption on hydrous ferric oxide. *Geochim. Cosmochim. Acta* 2003; **67**, 2551-60.

[13] SS Alharthi and HM Al-Saidi. Spectrophotometric determination of trace Concentrations of copper in waters using the chromogenic reagent 4-amino-3-mercapto-6-[2-(2-thienyl) vinyl]-1, 2, 4-triazin-5 (4H)-one: Synthesis, characterization, and analytical applications. *Appl. Sci*. 2020; **2020**, 3895.

[14] B Karabulut, A Bulut and R Tapramaz. An EPR study of Cu^{2+} doped sodium hydrogen oxalate monohydrate single crystal. *Spectrosc. Lett*. 1999; **32**, 571-9.

[15] R Kripal and S Misra. ESR of Cu^{2+} doped cadmium (II) formate dihydrate. *J. Phys. Chem. Solids* 2004; **65**, 939-48.

[16] CK Jorgensen. *Modern aspects of crystal field theory*. 1971.

[17] S Ravi and P Subramanian. Electron paramagnetic resonance and optical studies of Cu^{2+} doped bis(thiourea)cadmium chloride single crystal. *Solid State Sci.* 2007; **9**, 961-3.

[18] DS Schonland. On the determination of the principal g-values in electron spin resonance. *Proc. Phys. Soc.* 1959; **73**, 788.

[19] R Kripal and SD Pandey. EPR and optical absorption studies of Cu^{2+} doped lithium maleate dihydrate single crystal. *J. Phys. B: Condens. Matter* 2014; **444**, 14-20.

[20] R Kripal and DK Singh. ESR and optical study of Cu^{2+}-doped *Bis*(l-asparaginato)zinc(II). *J. Phys. Chem. Solids* 2006; **67**, 2559-66.
[21] D Srinivas, MVBLN Swamy and SEPR Subramanian. EPR of Cu(II) in dinitratobis(antipyrine)zinc (II) single crystals: A case of low symmetry and mixed ground state. *Mol. Phys.* 1986; **57**, 55-63.
[22] RPS Chakradhar, A Murali and JL Rao. A study of electron paramagnetic resonance and optical absorption spectra of VO^{2+} ions in alkali calcium borate glasses. *Phys. B: Condens. Matter* 2000; **293**, 108-17.
[23] UB Gangadharmath, SM Annigeri, AD Naik, VK Revankar and VB Mahale. Synthesis, characterisation and evaluation of molecular-orbital parameters, spin-orbit, dipolar and fermi-contact terms of VO^{2+} ion in thiosemicarbazone complexes. *J. Mol. Struct.: THEOCHEM* 2001; **572**, 61-71.
[24] HJ Prochaska, WF Schwindinger, M Schwartz, MJ Burk, E Bernarducci, RA Lalancette, JA Potenza and HJ Schugar. Characterization of apical copper(II)-thioether bonding. Structure and electronic spectra of bis(2,2-bis(5-phenyl-2-imidazolyl)propane)copper(II)diperchlorate and bis(1,3-bis(5-phenyl-2-imidazolyl)-2-thiapropane)copper(II) diperchlorate. *J. Am. Chem. Soc*. 1981; **103**, 3446-55.
[25] H Anandalakshmi, S Parthiban, V Parvathi, V Thanikachalam and SC Mojumdar. Thermal and optical properties of Cu (II)-doped magnesium rubidium sulfate hexahydrate crystals. *J. Therm. Anal. Calorim*. 2011; **104**, 963-7.
[26] R Elilarassi and G Chandrasekaran. Structural, optical and magnetic characterization of Cu-doped ZnO nanoparticles synthesized using solid state reaction method. *J. Mater. Sci. Mater. Electron.* 2010; **21**, 1168-73.