Preparation and characterization studies of metaborates, $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Ni, Co and Mn; $x = 0, 0.1$ and 0.5)

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Abstract. Copper metaborates of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Ni, Co and Mn; $x = 0, 0.1$ and 0.5) compositions are prepared using B_2O_3 flux. Powder XRD studies showed them all to belong to the tetragonal system with space group $I42d$. Their infrared spectra exhibit characteristic vibrational bands of BO_4 tetrahedron. The room temperature powder electron spin resonance (ESR) spectrum of copper metaborate gave a single peak at $g \approx 2.15$. The diffuse reflectance spectra (DRS) of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Ni, Co and Mn; $x = 0, 0.1$ and 0.5) are consistent with ligand to metal ion charge transfer and square planar symmetry of Cu^{2+} ion. The ligand field parameters Dq_{xy} , D_s and D_t are obtained.

Keywords. Powder XRD; infrared spectra; electron spin resonance; diffuse reflectance spectra.

1. Introduction

Transition metal and rare earth borates have long been the subject of interest over many decades due to their interesting crystal structures and potential applications (Bernal *et al* 1963; White *et al* 1965; Weidelt and Anorg 1970; Diehl 1975; Becker 1998; Knitel 1998; Keszler 1996, 1999; Boehm *et al* 2003). That boron can exist in planar BO_3 or tetrahedral BO_4 units leading to formation of poly borate rings gives rise to many structural possibilities. For instance, in FeBO_3 , boron exists in planar BO_3 while in Fe_3BO_6 it exists as tetrahedral BO_4 (Joubert *et al* 1968). On the other hand, both planar BO_3 and tetrahedral BO_4 units occur in LnB_3O_6 (Ln = trivalent rare earth ion) (Koteswara Rao *et al* 2002). Such variations in structures lead to interesting variations in their magnetic and optical properties as well. FeBO_3 is a room temperature ferromagnet and it is transparent in the visible region (Kurtzig *et al* 1969; Wolfe *et al* 1970) while Fe_3BO_6 is room temperature antiferromagnetic material and exhibits magnetic spin reorientation (Wolfe *et al* 1969; Kamzin and Bokov 1977). Keszler (1996, 1999) has reviewed the potential application of borates on account of their optical properties. For example, $\text{Eu}:\text{SrB}_4\text{O}_7$ is used as UV-emitting component in high-efficacy fluorescent lamps and $\text{Eu}(\text{Y},\text{Gd})\text{BO}_3$ as the red-emitting component in plasma display panels for high-definition television. Borate crystals such as (a) BiB_3O_6 , $\beta\text{-BaB}_2\text{O}_4$, LiB_3O_5 , and CsLiB_3O_6 are used as laser sources (Keszler 1996, 1999; Brenier *et al* 2002)

and (b) $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$, $\text{CsLiB}_6\text{O}_{10}$ and $\beta\text{-BaB}_2\text{O}_4$ exhibit excellent non-linear optical properties and find practical applications like powder tunable lasers and frequency mixers (Aka *et al* 1997; Yap *et al* 1998). The properties of these borates, however, depend on their purity. The conventional method of heating the stoichiometric amounts of reactants at high temperatures lead to inhomogeneity, impurity phases, defects and large distribution in the particle size. As a part of our search for better preparative methods, we have made an attempt to prepare copper meta borate and its solid solutions at temperatures much lower than reported using B_2O_3 flux. Boric acid melts at about 171°C and it does preserve the most desirable requirements as a reaction medium for borates. Several novel rare earth poly borates have been synthesized by this method (Lu *et al* 2001). In this paper, we report the preparation and characterization by X-ray, ESR and diffuse reflectance spectral studies of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Ni, Co and Mn; $x = 0, 0.1$ and 0.5) (compositions, hereafter abbreviated as CBM (x)).

2. Experimental

The earlier reported preparation of CBM ($x = 0$) involves annealing of the melt of stoichiometry, $\text{CuO}\cdot\text{B}_2\text{O}_3$, at 1000°C (Martinez-Ripoll *et al* 1971). Attempts to prepare CBM ($x = 0$) by this method always ended with impurities. Olaf Muller *et al* reported the preparation of FeBO_3 using B_2O_3 flux and the reaction time was reduced considerably by the addition of small amount of LiNO_3 or NaNO_3 (Olaf Muller *et al* 1978). We prepared CBM (x)

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compositions using this method. Stoichiometric amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_3BO_3 (400% excess), (AR grade chemicals) were dissolved in distilled water. To reduce the reaction time, 1 mole of NaNO_3 was added for every 50 moles of metal nitrates. The solution was slowly evaporated to dryness over a hot plate with constant stirring. The resultant mixture was ground thoroughly using spectral grade acetone to achieve greater homogeneity, dried and heated at $500^\circ\text{C}/5\text{ h}$ and $800^\circ\text{C}/10\text{ h}$ with intermediate grinding. The product was washed with distilled water to remove excess B_2O_3 and evaporated to dryness. Figure 1 gives the details of the procedure in the form of a flow chart.

For all compositions, powder X-ray diffractograms were recorded on Siemens D-4000 using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) and the data analysed using DBWS Rietveld refinement program (Young 1993). The infrared spectra were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer using KBr pellets. Room temperature ESR spectra were recorded on a JEOL PE-3X X-band spectrometer equipped with a 100 KHz field modulation unit using DPPH as standard. UV-Vis diffuse reflectance spectra of the samples were recorded using a Hitachi 3300H UV-Vis spectrometer in the 200–1100 nm range.

3. Results and discussion

3.1 Powder XRD

The powder X-ray diffractograms of all CBM (x) compositions are found to be similar (figure 2). The powder data

Figure 1. Flow chart for the preparation of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Co}$ and Mn ; $x = 0, 0.1$ and 0.5) by B_2O_3 flux method.

of CBM (x) were found to be in close agreement with those reported earlier free from any impurity phases (Martinez-Ripoll *et al* 1971). A typical Rietveld fitted XRD patterns of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$ and $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$ are given in figures 3 and 4, respectively.

The d -lines of $\text{Cu}_{0.9}\text{Ni}_{0.1}\text{B}_2\text{O}_4$ and $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$ are similar to each other and similar to that of CuB_2O_4 . Thus,

Figure 2. Powder X-ray diffraction patterns of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Mn}, \text{Co}$ and Ni ; $x = 0, 0.1$ and 0.5).

Figure 3. Experimental (---), calculated (—) and difference profile of the XRD pattern of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$.

these two compositions are isomorphous with CuB_2O_4 . In view of the non-existence of NiB_2O_4 , the solid solution range in the system, $\text{Cu}_{1-x}\text{Ni}_x\text{B}_2\text{O}_4$, could be obtained only by trial. Though the powder XRD of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$ does not show any impurity lines, its infrared spectrum shows a small peak around $1200\text{--}1400\text{ cm}^{-1}$ which is characteristic of planar BO_3 group. This may be due to the onset of formation of phases such as $\text{Ni}_3(\text{BO}_3)_2$ in trace quantities having isolated planar $[\text{BO}_3]^{3-}$ units (Pardo *et al* 1974). Thus the compositional range in the $\text{Cu}_{1-x}\text{Ni}_x\text{B}_2\text{O}_4$ system is also found to be limited to $0 \leq x < 0.5$. In the case of $\text{Cu}_{1-x}\text{Mn}_x\text{B}_2\text{O}_4$ and $\text{Cu}_{1-x}\text{Co}_x\text{B}_2\text{O}_4$ systems, the end members viz. MnB_2O_4 and CoB_2O_4 , have been reported (The Dow Chemical Company; New Jersey Zinc Company). However, their detailed crystal structure data have not been reported so far. A close comparison of d -lines of MnB_2O_4 and CoB_2O_4 with that of CuB_2O_4 shows that these systems are not isomorphous. Hence, complete solid solutions in the systems (a) $\text{Cu}_{1-x}\text{Mn}_x\text{B}_2\text{O}_4$ and (b) $\text{Cu}_{1-x}\text{Co}_x\text{B}_2\text{O}_4$ may be ruled out. The d -lines of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Mn}$ and Co ; $x = 0.1$ and 0.5), however, are similar to that of CuB_2O_4 and therefore, isomorphous with it. Attempts to substitute with $x > 0.5$ led to impurity phases. Thus the compositional range in these two systems do exist atleast up to $x = 0.5$.

Copper meta borate (CuB_2O_4) crystallizes in tetragonal lattice with space group $I4_2d$ and each unit cell contains 12 molecules of CuB_2O_4 . The oxygens occupy $16e$ and $8d$ sites while boron is located at $16e$ and $8d$ sites. The divalent copper occupies two crystallographic sites, viz. $4b$ and $8d$ with a relative ratio of 1 : 2. Thus the crystallographic formula of copper meta borate per unit cell can be written as $[\text{Cu}_{10.8}\text{M}_{1.2}\text{B}_{24}\text{O}_{48}]$. The molecular formula per unit cell of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$ and $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$ are $\text{Cu}_{10.8}\text{M}_{1.2}\text{B}_{24}\text{O}_{48}$ and $\text{Cu}_6\text{M}_6\text{B}_{24}\text{O}_{48}$, respectively. In Cu_{1-x}

$\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Mn}$, Co and Ni ; $x = 0.1$ and 0.5) compositions, the site occupancy of both Cu and M is obtained in the following way.

In the first step it is assumed that M and Cu ions occupy $4b$ and $8d$ sites and the positions of the rest of the atoms unchanged. The Rietveld analysis of this combination gave acceptable R values. In the next step, the occupancies of M and Cu ions are changed within the $4b$ and $8d$ sites for further refinement. It is observed that good agreement between the experimental and calculated XRD patterns was obtained when (a) copper ions occupy 90% of $4b$ and $8d$ sites while M ions occupy the remaining 10% of $4b$ and $8d$ sites in the case of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$ and (b) copper and M ions occupy 50% each of $4b$ and $8d$ sites for $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$. Thus the crystallographic formula of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$ and $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$ is $[\text{Cu}_{3.6}\text{M}_{0.4}]_{4b}[\text{Cu}_{7.2}\text{M}_{0.8}]_{8d}\text{B}_{24}\text{O}_{48}$ and $[\text{Cu}_2\text{M}_2]_{4b}[\text{Cu}_4\text{M}_4]_{8d}\text{B}_{24}\text{O}_{48}$, respectively. The final reliability factors and atomic parameters obtained from Rietveld refinement for $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$ and $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$ are given in tables 1–4. The a and c values obtained for all the CBM (x) compositions are given in table 5 and these values are found to be close to each other as well as with those reported earlier for CuB_2O_4 (Martinez-Ripoll *et al* 1971). The observed and calculated d -values are given in tables 6 and 7 for all the compositions. The small variations in the unit cell parameters are attributed to the variations of ionic size of doped M^{2+} . The structure of these solid solutions is similar to that of CuB_2O_4 with the substituted metal ion ($\text{Ni}^{2+}/\text{Co}^{2+}/\text{Mn}^{2+}$) occupying the copper sites.

3.2 IR spectra

The infrared spectra of all the compositions under investigation are shown in figures 5 and 6. It is noticed from

Figure 4. Experimental (---), calculated (—) and difference profile of the XRD pattern of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$.

Table 1. Results of the Rietveld analysis of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$.

Formula	$\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$
Profile fit	Pseudo-Voigt
Density (calculated)/ g/cm^3	4.00
Space group	$I4_2d$
Lattice parameters	
$a = b(\text{\AA})$	11.482
$c(\text{\AA})$	5.606
$\alpha, \beta, \gamma(^{\circ})$	90
$V(10^6 \text{ pm}^3)$	738.887
Coefficients for peak FWHM	
U	0.000
V	0.000
W	0.10(1)
Conventional Rietveld R -factors	
R (expected) (%)	4.8
R (profile) (%)	7.7
R (weighted profile) (%)	10.2
R (Bragg) (%)	4.2

Table 2. Occupancy, atomic fractional coordinates and isotropic displacement parameters of $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$.

Atom	Wyck.	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (10 ⁴ pm ²)
Cu1	4 <i>b</i>	0.900000	0.000000	0.000000	0.500000	0.750000
Mn1	4 <i>b</i>	0.100000	0.000000	0.000000	0.500000	0.750000
Cu2	8 <i>d</i>	0.900000	0.081500	0.250000	0.125000	0.759980
Mn2	8 <i>d</i>	0.100000	0.081500	0.250000	0.125000	0.759980
O1	16 <i>e</i>	1.000000	0.158950	0.070790	0.498100	0.200000
O2	8 <i>d</i>	1.000000	0.252790	0.250000	0.625000	0.200000
O3	8 <i>d</i>	1.000000	0.250000	0.082690	0.875000	0.879980
O4	16 <i>e</i>	1.000000	0.074500	0.188960	0.795580	0.200000
B1	16 <i>e</i>	1.000000	0.183770	0.148350	0.699190	0.100000
B2	8 <i>d</i>	1.000000	0.998880	0.250000	0.625000	0.100000

Table 3. Results of the Rietveld analysis of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$.

Formula	$\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$
Profile fit	Pseudo-Voigt
Density (calculated) (g/cm ³)	3.88
Space group	<i>I</i> 42 <i>d</i>
Lattice parameters	
<i>a</i> = <i>b</i> (Å)	11.511
<i>c</i> (Å)	5.613
α , β , γ (°)	90
<i>V</i> (10 ⁶ pm ³)	743.427
Coefficients for peak FWHM	
U	0.000
V	0.000
W	0.14(2)
Coefficients for peak FWHM	
<i>R</i> (expected) (%)	5.6
<i>R</i> (profile) (%)	4.2
<i>R</i> (weighted profile) (%)	4.8
<i>R</i> (Bragg) (%)	5.0

these figures that all the bands observed are below 1150 cm⁻¹ except in the case of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$. In the infrared spectrum of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$, an additional peak of relatively small intensity around 1200–1400 cm⁻¹ is observed. These IR spectra are similar to that of earlier reported borates containing BO₄ tetrahedra (Herzberg 1949; Joubert *et al* 1968; Martinez-Ripoll *et al* 1971). The band positions along with their assignments are given in table 8 for all the compositions.

In general, borates are characterized by complex anions that arise from polymerization of (a) planar BO₃ or (b) tetrahedral BO₄ or (c) both BO₃ and BO₄ units. For an isolated planar trigonal BO₃ group of *D*_{3h} symmetry six fundamental modes of vibrations are expected (Weir and Lippincott 1961). They are ν_1 (symmetric stretch, non-degenerate, 950 cm⁻¹), ν_2 (out of plane bending, non-degenerate, 750 cm⁻¹), ν_3 (antisymmetric stretch, doubly degenerate, 1250 cm⁻¹) and ν_4 (in plane bending, doubly degenerate, 600 cm⁻¹) (Weir and Lippincott 1961). Tetrahedral BO₄ group gives nine fundamental modes of vibrations and are given by ν_1 (symmetric stretch, non-

Figure 5. IR spectra of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Mn, Co and Ni; *x* = 0 and 0.1).

degenerate, 1000 cm⁻¹), ν_2 (bond bending, doubly degenerate, below 950 cm⁻¹), ν_3 (stretching mode, triply degenerate, near 600 cm⁻¹) and ν_4 (bending mode, triply degenerate, below 600 cm⁻¹) (Herzberg 1949). In borates, the strong infrared band at 1250 cm⁻¹ (ν_3) is used as a diagnostic tool to identify the type of boron coordination.

Table 4. Occupancy, atomic fractional coordinates and isotropic displacement parameters of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$.

Atom	Wyck.	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (10 ⁴ pm ²)
Cu1	4 <i>b</i>	0.500000	0.000000	0.000000	0.500000	0.750000
Mn1	4 <i>b</i>	0.500000	0.000000	0.000000	0.500000	0.750000
Cu2	8 <i>d</i>	0.500000	0.081500	0.250000	0.125000	0.759980
Mn2	8 <i>d</i>	0.500000	0.081500	0.250000	0.125000	0.759980
O1	16 <i>e</i>	1.000000	0.158950	0.070790	0.498100	0.200000
O2	8 <i>d</i>	1.000000	0.252790	0.250000	0.625000	0.200000
O3	8 <i>d</i>	1.000000	0.250000	0.082690	0.875000	0.879980
O4	16 <i>e</i>	1.000000	0.074500	0.188960	0.795580	0.200000
B1	16 <i>e</i>	1.000000	0.183770	0.148350	0.699190	0.100000
B2	8 <i>d</i>	1.000000	0.998880	0.250000	0.625000	0.100000

Table 5. Lattice parameters of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Mn, Co and Ni; *x* = 0, 0.1 and 0.5).

Compound	Lattice parameters		Reference
	<i>a</i> (Å)	<i>c</i> (Å)	
CuB_2O_4	11.461	5.612	Present work
$\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$	11.482	5.606	Present work
$\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$	11.511	5.613	Present work
$\text{Cu}_{0.9}\text{Co}_{0.1}\text{B}_2\text{O}_4$	11.531	5.591	Present work
$\text{Cu}_{0.5}\text{Co}_{0.5}\text{B}_2\text{O}_4$	11.500	5.625	Present work
$\text{Cu}_{0.9}\text{Ni}_{0.1}\text{B}_2\text{O}_4$	11.451	5.601	Present work
$\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$	11.485	5.621	Present work

This band will be observed in borates containing planar BO_3 groups and will be absent in borates having only tetrahedral BO_4 groups. The absence of a band at 1250 cm^{-1} in the present samples clearly indicates that boron is in tetrahedral coordination (BO_4). In the case of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$, the band observed in the range $1200\text{--}1400\text{ cm}^{-1}$ belongs to planar BO_3 group presumably of an impurity phase, $\text{Ni}_3(\text{BO}_3)_2$, formed along with nickel doped copper metaborate.

3.3 ESR spectra

Room temperature powder ESR spectrum of CBM (*x* = 0) is shown in figure 7. A symmetric broad ESR signal with $g \approx 2.15$ is obtained for this sample. The Cu^{2+} ion with $3d^9$ configuration is expected to give single or four line ESR spectrum for each of chemically/crystallographically inequivalent site as a result of one unpaired electron ($S = 1/2$) interacting with applied magnetic field and also with nuclear spin of ^{63}Cu ($I = 3/2$). If Cu^{2+} is doped in a diamagnetic lattice, it is expected to give four-line ESR spectrum in single crystal or less frequently in powder form. Undiluted powder samples invariably give broad ESR signal while diluted samples give either broad single line ESR spectrum or four-line resolved ESR spectra. In CBM (*x* = 0), divalent copper is in two crystallographically inequivalent sites (Martinez-Ripoll *et al* 1971).

Figure 6. IR spectra of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ (M = Mn, Co and Ni; *x* = 0.5).

$\text{Cu}(1)$ is characterized by a square planar geometry with Cu–O distance of 1.999 Å . $\text{Cu}(2)$ is surrounded by four oxygens (with distances of 1.886 , 1.98 , 1.9 , 1.98 Å) in plane and two oxygens, one above and one below the plane at a distance of 3.069 Å forming elongated distorted octahedral coordination (Martinez-Ripoll *et al* 1971). Since the axial oxygens are farther away from central copper, it can be considered as distorted square planar geometry. The symmetric broad ESR signal with $g \approx 2.15$ with peak to peak width of ≈ 110 gauss observed in CBM

Table 6. Observed and calculated d spacing values of $\text{Cu}_{1-x}\text{Mn}_x\text{B}_2\text{O}_4$ ($x = 0, 0.1$ and 0.5).

Composition	CuB_2O_4		$\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$		$\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$	
hkl	$d_{\text{obs}} (\text{\AA})$	$d_{\text{cal}} (\text{\AA})$	$d_{\text{obs}} (\text{\AA})$	$d_{\text{cal}} (\text{\AA})$	$d_{\text{obs}} (\text{\AA})$	$d_{\text{cal}} (\text{\AA})$
2 0 0	5.6822	5.7420	5.7020	5.7484	5.7223	5.7484
1 0 1	5.0023	5.0382	5.0378	5.0491	5.0255	5.0447
2 2 0	4.0364	4.0602	4.0572	4.0647	4.0528	4.0647
2 1 1	3.7757	3.7871	3.7842	3.7935	3.7845	3.7917
3 1 0	3.6153	3.6316	3.6303	3.6356	3.6320	3.6356
3 0 1	3.1538	3.1614	3.1637	3.1662	3.1604	3.1651
4 0 0	2.8620	2.8710	2.8734	2.8742	2.8726	2.8742
3 2 1	2.7648	2.7648	2.7706	2.7734	2.7710	2.7726
1 1 2	2.6482	2.6482	2.6507	2.6559	2.6506	2.6533
4 2 0	2.5629	2.5679	2.5696	2.5708	2.5708	2.5708
4 1 1	2.4886	2.4944	2.4982	2.4978	2.4965	2.4973
3 1 2	2.2182	2.2191	2.2195	2.2233	2.2216	2.2218
4 3 1	2.1222	2.1254	2.1272	2.1281	2.1289	2.1278
4 4 0	2.0036	2.0057	2.0080	2.0324	2.0077	2.0324
5 3 0	1.9666	1.9695	—	1.9717	—	1.9717
4 2 2	1.8922	1.8935	1.8941	1.8968	1.8963	1.8958
1 0 3	1.8463	1.8446	1.8459	1.8490	1.8454	1.8470
6 2 0	1.8134	1.8158	1.8173	1.8178	1.8194	1.8178
6 1 1	1.7873	1.7892	1.7915	1.7915	1.7907	1.7913
2 1 3	1.7571	1.7562	1.7568	1.7602	1.7586	1.7585
5 4 1	1.7072	1.7082	1.7111	1.7103	1.7115	1.7102
6 2 2	1.5237	1.5237	1.5277	1.5263	1.5260	1.5258
5 2 3	1.4058	1.4058	1.4082	1.4081	1.4084	1.4072
7 4 1	1.3809	1.3806	1.3868	1.3822	1.3851	1.3821
7 2 3	1.2064	1.2054	1.2018	1.2074	1.2068	1.2069
8 5 1	1.1897	1.1896	—	1.1910	—	1.1909
6 0 4	1.1328	1.1308	1.1334	1.1331	1.1326	1.1323

Figure 7. ESR spectrum of CuB_2O_4 .

($x = 0$) is characteristic of undiluted nature of copper and the two sites of copper are not distinguishable in the powder form.

3.4 Diffuse reflectance spectra

The diffuse reflectance spectra of CBM (x) in the region 200–1100 nm are shown in figures 8 and 9. All the spec-

tra exhibit absorption bands in the regions 250–400 nm (band A) and at 460–900 nm (band B) (figures 8 and 9). The B band is asymmetric and less intense compared to the A band. The B band could be decomposed into three Gaussians for CBM ($x = 0$) (figure 10) and CBM ($x = 0.1$). The band maxima of these three Gaussians are shown in table 9. The diffuse reflectance spectrum of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$ is slightly different from that of $x = 0.1$ compositions. The B band maximum for this composition is in the range 450–800 nm with shoulder on the lower wavelength side (figure 9). The analysis of CBM ($x = 0.1$) compositions is based on the fact that the observed optical spectral features are due entirely to Cu^{2+} ions only as its concentration is 90%.

The A band observed in all the compositions may be due to ligand to metal charge transfer transition (Hathaway and Billing 1970). The asymmetric B band observed in the region 460–900 nm is due to forbidden $d-d$ transitions. The local symmetry of Cu^{2+} in CBM (x) is square planar as discussed earlier. For Cu^{2+} ion in square planar geometry, the $d-d$ transitions are given by (Kobinata 1974)

$$\nu_1(^2A_{1g} \leftarrow ^2B_{1g}) = 4D_s + 5D_t, \quad (1)$$

$$\nu_2(^2B_{2g} \leftarrow ^2B_{1g}) = 10Dq_{xy}, \quad (2)$$

$$\nu_3(^2E_g \leftarrow ^2B_{1g}) = 10Dq_{xy} + 3D_s - 5D_t, \quad (3)$$

Table 7. Observed and calculated d spacing values of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Co}$ and Ni ; $x = 0.1$ and 0.5).

hkl	$\text{Cu}_{0.9}\text{Co}_{0.1}\text{B}_2\text{O}_4$		$\text{Cu}_{0.5}\text{Co}_{0.5}\text{B}_2\text{O}_4$		$\text{Cu}_{0.9}\text{Ni}_{0.1}\text{B}_2\text{O}_4$		$\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$	
	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$
2 0 0	5.7367	5.7446	5.7197	5.7420	5.7107	5.7420	—	5.7420
1 0 1	5.0386	5.0457	5.0300	5.0415	5.0312	5.0405	—	5.0490
2 2 0	4.0508	4.0620	5.0598	4.0602	4.0411	4.0602	4.0596	4.0602
2 1 1	3.7879	3.7910	3.7789	3.7885	3.7765	3.7880	3.7743	3.7917
3 1 0	3.6301	3.6332	3.6184	3.6316	3.6183	3.6316	3.6268	3.6316
3 0 1	3.1603	3.1641	3.1559	3.1622	3.1550	3.1620	—	3.1641
4 0 0	2.8714	2.8723	2.8650	2.8710	2.8645	2.8710	2.8695	2.8710
3 2 1	2.7686	2.7715	2.7647	2.7699	2.7647	2.7698	2.7691	2.7712
1 1 2	2.6532	2.6541	2.6487	2.6517	2.6477	2.6512	2.6523	2.6561
4 2 0	2.5679	2.5690	2.5645	2.5679	2.5634	2.5679	—	2.5679
4 1 1	2.4939	2.4962	2.4893	2.4948	2.4896	2.4947	2.4929	2.4957
3 1 2	2.2220	2.2218	2.2174	2.2202	2.2185	2.2198	2.2224	2.2228
4 3 1	2.1255	2.1267	2.1219	2.1256	2.1233	2.1255	2.1266	2.1262
4 4 0	2.0302	2.0310	2.0032	2.0066	2.1255	2.0301	1.9907	2.0301
5 3 0	1.9704	1.9704	1.9670	1.9695	1.9684	1.9695	—	1.9695
4 2 2	1.9008	1.8955	1.8921	1.8942	1.8927	1.8940	1.8962	1.8958
1 0 3	1.8472	1.8477	1.8455	1.8460	1.8463	1.8456	—	1.8494
6 2 0	1.8161	1.8166	1.8147	1.8158	1.8146	1.8158	—	1.8158
6 1 1	1.7905	1.7903	1.7880	1.7894	1.7880	1.7893	1.7918	1.7897
2 1 3	1.7575	1.7590	1.7571	1.7574	1.7564	1.7571	1.7582	1.7603
5 4 1	1.7087	1.7092	1.7073	1.7084	1.7077	1.7083	1.7133	1.7086
6 2 2	1.5257	1.5253	1.5239	1.5244	1.5245	1.5243	1.5293	1.5252
5 2 3	1.4070	1.4072	1.4067	1.4061	1.4067	1.4060	1.4091	1.4076
7 4 1	1.3820	1.3813	1.3820	1.3823	1.3814	1.3820	—	1.3808
7 2 3	1.2074	1.2066	1.2065	1.2058	1.2073	1.2057	—	1.2068
8 5 1	1.1908	1.1902	1.1907	1.1896	1.1903	1.1896	—	1.1897
6 0 4	1.1334	1.1339	1.1335	1.1332	1.1328	1.1313	—	1.1328

Table 8. IR spectral data of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Mn}$, Co and Ni ; $x = 0$, 0.1 and 0.5 ; the band positions are in cm^{-1}).

Compositions							Approximate type of motion
CuB_2O_4	$\text{CBMn}_{0.1}$	$\text{CBMn}_{0.5}$	$\text{CBCo}_{0.1}$	$\text{CBCo}_{0.5}$	$\text{CBNi}_{0.1}$	$\text{CBNi}_{0.5}$	
1138vs	1139vs	1138vs	1139vs	1139vs	1138vs	1138vs	$\nu_1(\text{PO}_4)$
1038vs	1037vs	1037vs	1038vs	1038vs	1039vs	1038vs	
989vs	987vs	1088vs	988vs	988vs	988vs	989vs	
952vs	952vs	952vs	952vs	947vs	952vs	953vs	$\nu_2(\text{PO}_4)$
909s	906s	906s	906s	905vs	906vs	905s	
866s	859s	862s	862s	861vs	862vs	864s	
697m	693m	694m	694m	694m	694m	694m	$\nu_3(\text{PO}_4)$
624w	621w	621w	621w	622w	623w	620w	
427w	426w	425w	424w	424w	426w	422w	$\nu_4(\text{PO}_4)$

vs = very sharp, s = sharp, m = medium, w = weak

where Dq_{xy} and D_t are one electron radial integrals of the fourth order in r , the d -orbital distance from the Cu^{2+} nucleus. D_s the corresponding second order integral. Dq_{xy} is a measure of the strength of the ligand field. D_t and D_s express the tetragonal components of the ligand field. From (1)–(3), it follows that

$$4\nu_3 = 2\nu_2 + 3\nu_1, \quad (4)$$

and

$$D_t/D_q = 4/7. \quad (5)$$

The possible band assignments for B band are verified with (4). Among all the possible combinations, two combinations (combinations (1) and (2), table 9) give reasonable estimations of Dq_{xy} , D_s and D_t parameters. These combinations and the derived parameters for Dq_{xy} , D_s and D_t are given in table 9 along with the parameters of Cu^{2+} ion in different lattices having square planar geometry. The ligand field parameters are consistent with other copper complexes having Cu^{2+} in square planar geometry (table 9). For square planar Cu^{2+} complexes, the ratio D_t/D_q is equal to $4/7$ or 0.571 (5). In the present investi-

Table 9. Band assignments and ligand field parameters of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Mn, Co and Ni}$; $x = 0, 0.1$ and 0.5).

Composition	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Dq_{xy}	D_s	D_t	D_t/D_q	D_q/D_s	Reference
CuB_2O_4									
(1)	12050	13550	16300	1355	2114	719	0.53	0.64	Present work
(2)	13550	12050	16300	1205	2543	676	0.56	0.47	
(3)	16300	12050	13550	1205	2543	1226	1.01	0.47	
$\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$									
(1)	13550	15600	17250	1560	2171	973	0.62	0.72	Present work
(2)	15600	13550	17250	1355	2757	914	0.67	0.49	
(3)	17250	13550	15600	1355	2757	1244	0.92	0.49	
$\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$									
(1)	13700	15910	18250	1591	2291	907	0.57	0.69	Present work
(2)	15910	13700	18250	1370	2922	844	0.62	0.47	
(3)	18250	13700	15910	1370	2922	1312	0.96	0.47	
$\text{Cu}_{0.9}\text{Co}_{0.1}\text{B}_2\text{O}_4$									
(1)	12350	14450	17000	1445	2128	768	0.53	0.68	Present work
(2)	14450	12350	17000	1235	2728	708	0.57	0.45	
(3)	17000	12350	14440	1235	2728	1218	0.97	0.45	
$\text{Cu}_{0.5}\text{Co}_{0.5}\text{B}_2\text{O}_4$									
(1)	12540	14200	16820	1420	2166	775	0.54	0.65	Present work
(2)	14200	12540	16820	1254	2640	728	0.58	0.47	
(3)	16820	12540	14200	1254	2640	1252	0.99	0.47	
$\text{Cu}_{0.9}\text{Ni}_{0.1}\text{B}_2\text{O}_4$									
(1)	13800	16350	18650	1635	2300	920	0.56	0.71	Present work
(2)	16350	13800	18650	1380	3028	848	0.61	0.45	
(3)	18650	13800	16350	1380	3028	1308	1.00	0.45	
$\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$									
(1)	14290	16700	18980	1670	2367	964	0.58	0.70	Present work
(2)	16700	14290	18980	1429	3056	895	0.62	0.47	
(3)	18980	14290	16700	1429	3056	1351	0.94	0.47	
$\text{Cu}(\text{H}_2\text{O})_4^{2+}$ on montmorillonite									
(1)	10550	13100	15200	1310	1807	664	0.51	0.72	(Velghe et al 1977)
(2)	13100	10550	15200	1055	2535	591	0.56	0.42	
(3)	15200	10550	13100	1055	2535	1011	0.96	0.42	
$\text{Cu}(\text{H}_2\text{O})_4(\text{HCO}_2)_2$	9200	11200	13200	1120	1600	560	0.50	0.70	Do
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	10500	13000	14500	1300	1714	729	0.56	0.76	Do

Figure 8. Diffuse reflectance spectra of (a) CuB_2O_4 , (b) $\text{Cu}_{0.9}\text{Mn}_{0.1}\text{B}_2\text{O}_4$, (c) $\text{Cu}_{0.9}\text{Co}_{0.1}\text{B}_2\text{O}_4$ and (d) $\text{Cu}_{0.9}\text{Ni}_{0.1}\text{B}_2\text{O}_4$.

gation, this ratio is close to 0.57 for CBM (x) compositions confirming the square planar geometry for central copper ion (table 9).

The B band of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$ shows a hypsochromic shift with shoulders on either side of the band maximum. The Ni^{2+} ($3d^8$) in square planar geometry generally gives (i) a single broad band at $18000\text{--}25000\text{ cm}^{-1}$ which can be decomposed into three bands by Gaussian analysis or (ii) broad band with weak shoulder on each side of the band (Lever 1984a). In the case of the diffuse reflectance spectrum of $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$, the broad band observed in the region $12500\text{--}22200\text{ cm}^{-1}$ is due to both Ni^{2+} and Cu^{2+} in square planar coordination. The diffuse reflectance spectrum of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{B}_2\text{O}_4$ is similar to that of CBM ($x = 0$ and 0.1). Square planar Co^{2+} complexes exhibit several transitions in the region $3900\text{--}7000\text{ cm}^{-1}$, a multiplet of three bands at $8300\text{--}11000\text{ cm}^{-1}$ and several transitions in the visible region $14000\text{--}20000\text{ cm}^{-1}$ (Lever 1984b). The visible transition is overlapped with Cu^{2+} transitions. Therefore, the B band of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{B}_2\text{O}_4$ ob-

served in the region 460–900 nm is due to both Cu^{2+} and Co^{2+} in square planar geometry. The diffuse reflectance spectrum of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$ is also similar to that of CBM ($x = 0$ and 0.1) but with less intensity. The Mn^{2+} with $3d^5$ configuration gives very weak transitions in the visible region. Thus the observed less intense *B* band arises due to Cu^{2+} in square planar coordination only.

4. Conclusions

Copper meta borate in the parent form and in the substituted phases replacing copper by nickel, cobalt and manga-

nese leading to solid solutions of the formulae, $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ ($\text{M} = \text{Ni}, \text{Co}$ and Mn ; $x = 0, 0.1$ and 0.5) could be prepared at low temperatures using B_2O_3 flux. Attempts to substitute with $x > 0.5$ led to impurity phases. XRD studies showed that the parent compound and the solid solutions are isomorphous crystallizing in the tetragonal lattice with space group $I4_2d$. Infrared spectral evidence showed that boron existed exclusively as BO_4 tetrahedra in all the cases. Electron spin resonance is characteristic of undiluted divalent copper in square planar symmetry with strong metal–metal interaction. Diffuse reflectance spectra of $\text{Cu}_{1-x}\text{M}_x\text{B}_2\text{O}_4$ show ligand to metal charge transfer band and $d-d$ transitions of Cu^{2+} . The ligand field parameters for Cu^{2+} in square planar coordination have been derived from the optical spectra.

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Figure 9. Diffuse reflectance spectra of (e) $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{B}_2\text{O}_4$, (f) $\text{Cu}_{0.5}\text{Co}_{0.5}\text{B}_2\text{O}_4$ and (g) $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{B}_2\text{O}_4$.

Figure 10. Decomposition into three Gaussian bands of the diffuse reflectance spectrum of Cu^{2+} in CuB_2O_4 .

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