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Optical Properties of Pure and Modified Copper Tartrate Single Crystals

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Abstract: *Single crystals of tartrate compounds are of great interest on account of their excellent optoelectronic properties. These properties explore the possibility of tartrate compounds to be exploited for various device applications. This has attracted the attention of researchers to grow single crystals of tartrate compounds and study their properties. The present work reports the optical properties of pure and sodium modified copper tartrate single crystals. Single crystal growth of these materials followed by their characteristics has already been published somewhere else. Having achieved the growth of pure and sodium modified copper tartrate single crystals and established their basic characteristics, it is thought worthwhile to have an understanding of their optical properties and their modification on replacement of some copper ions in the lattice of copper tartrate by sodium ions.*

Keywords: Single Crystal, Optical Properties, Colour Centres, Optoelectronic materials, Doping

I. Introduction

Single crystals of tartrate compounds are of great interest due to their excellent optoelectronic properties [1-6]. These properties explore the possibility of tartrate compounds to be exploited for various device applications. This has attracted the attention of several workers to grow single crystals of tartrate compounds and study their properties [7-10]. The present paper reports the optical properties of pure and sodium modified copper tartrate single crystals. Single crystal growth by gel method of these materials followed by their characteristics has already been published somewhere else [11]. Colour centres are defects in crystals in the form of cation vacancies [12]. These defects are aptly named so as they are responsible for the colour of normally transparent crystals. The absence of the negative ion acts like a positive hole that can attract and trap an electron. The trapped electron is in a bound state with characteristic energy levels. These defects absorb light of a broad range of wavelengths depending upon the spacing of energy levels of the electron trapped in that colour centre.

Optical transitions between the bound states of the trapped electron cause the colouration of the crystals. Materials with colour centres have broad absorption and emission spectrum that enables their applications in radiation dosimeters, memory devices and for construction of tunable lasers. It is reported in the literature that materials with colour centre can serve as excellent tunable laser source [13]. Therefore, it is quite useful to devise a material with such type of optical properties that can serve as a suitable potential material in modern industry. The vacancies are typically created by introducing excess of metal ions or by heating or by doping. Metal ion doped materials are currently receiving a great deal of attention due to the rapid development of laser diodes [14]. It is reported in the literature that presence of foreign metal ions in the parent compound affects the whole growth process and physical properties due to the difference in the ionic radius and electric charge [15].

II. Experimental Procedure

Optical absorption spectra of the grown crystals were recorded at room temperature in the wavelength range of 200 to 800 nm using Varian Cary 5000 UV-VIS-NIR spectrometer covering the entire ultraviolet and visible regions

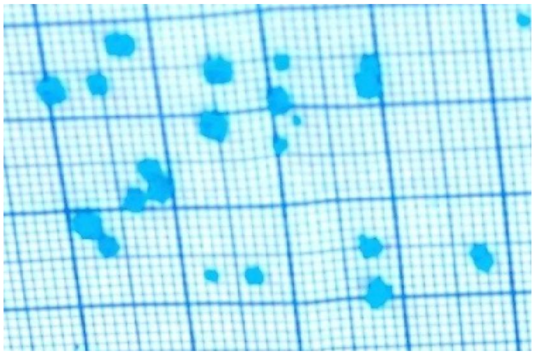
III. Results and Discussion

Single crystals of pure and sodium modified copper tartrate grown by gel encapsulation technique assume orthorhombic and tetragonal symmetry with space groups $P2_12_12_1$ and $P4_2/$ nbc respectively. The same has been worked out by selecting intense peaks of diffractograms using CRYSFIRE software. The stoichiometric composition of pure crystals is $CuC_4H_4O_6.3H_2O$ whereas that of modified ones is $(Cu)_{0.77}$ $(Na)_{0.23}C_4H_4O_6.3H_2O$ and $(Cu)_{0.65}$ $(Na)_{0.35}$ $C_4H_4O_6.H_2O$. The stoichiometric composition of the crystals has been determined using C-H analysis, EDAX, FTIR supplemented by thermoanalytical techniques. The maximum size of pure copper tartrate crystals is 4.5 mm x 4 mm x 3 mm whereas that of modified copper tartrate crystals is 3mm x 2.5 mm x 2 mm. The details of these results have already been published [11]. Fig. 1 shows the optical micrographs of the grown crystals revealing their characteristic colour and size

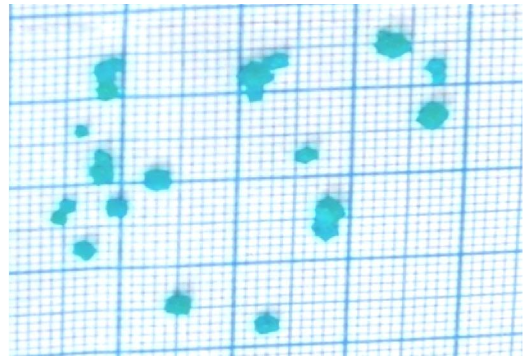
3.1 Optical Characteristics

Optical behaviour of pure and modified copper tartrate single crystals was studied by recording absorption spectra in the wavelength range of 200 to 800 nm that covers the entire ultraviolet and visible region. The plots of absorbance against wavelength for all the three compositions (pure and modified) are shown in fig. 2. From the figure it is clear that transmittance is more than 80 % for both pure and modified copper tartrate crystals for a particular range of wavelengths. The value of this range is 422-556 nm for pure crystals of composition $CuC_4H_4O_6.3H_2O$ and 441-560 nm and 459-553 nm for substituted crystals bearing composition $(Cu)_{0.77}$ $(Na)_{0.23}C_4H_4O_6.3H_2O$ and $(Cu)_{0.65}$ $(Na)_{0.35}$ $C_4H_4O_6.H_2O$ respectively. These broad ranges of wavelengths where the absorption is negligible indicate the existence of colour centres in these materials. Fig. 1 depicts the colour of pure and modified copper tartrate single crystals. Pure crystals are blue green in colour whereas the doped ones are green in colour. Table 1 provides the colour and corresponding value of range of wavelengths for the crystals of pure and modified copper tartrate. A closer look at the values of wavelength ranges of pure and modified copper tartrate crystals indicates that the upper limit of wavelength is almost same for both pure and modified crystals but there is a great difference between the values of lower limit of wavelengths for these materials. This indicates that on modifying pure crystals by Na^+ ions there is a shift in the value of wavelengths which is responsible for the change in colour of pure crystals. The existence of colour centres in copper tartrate crystals and shift in the range of wavelengths on modification by Na^+ ions is explained below.

When light encounters a material it interacts with it in different ways. These interactions depend on the nature of light and the nature of substance. Certain substances do not absorb light and appear to be transparent whereas some substances absorb light and appear to be opaque. There are some other substances that are selective in their absorption of light of particular frequencies while reflecting others depending on their chemical composition. These frequencies that are not being absorbed and are transmitted or reflected are responsible for the colour of that substance [16]. Such substances have a chemical composition that includes what are referred to as absorption centres. The existence of colour in pure and modified copper tartrate crystals may be explained on the basis of existence of colour centre in these materials. Mechanism of selective absorption is due to the transition of electron in energy levels of an atom. An electron under impact by an incident photon is excited to an intermediate state where it interacts with lattice vibrations and impurities before it reaches a final state, the net result being the absorption of photons [17]. Doping also plays an important role in the phenomenon of colour centres. Production of colour by a material depends on the nature of foreign ions. In the present study doping of copper tartrate by Na^+ ions leads to a shift in the value of range of wavelengths for which the material remains transparent to the incident light. This may be due to the fact that modification of pure copper tartrate by Na^+ ions leads to a change in the crystal system of the material and consequently there is a change in the energy levels of electrons of the constituent atoms in the material. As a result, modified copper tartrate is transparent to light waves of different range of wavelengths. A comparison of values of range of wavelengths for pure and modified crystals is given in table 1.



(a) Pure crystals



(b) Modified crystals

Figure 1: Optical photograph showing crystals of pure and modified copper tartrate.

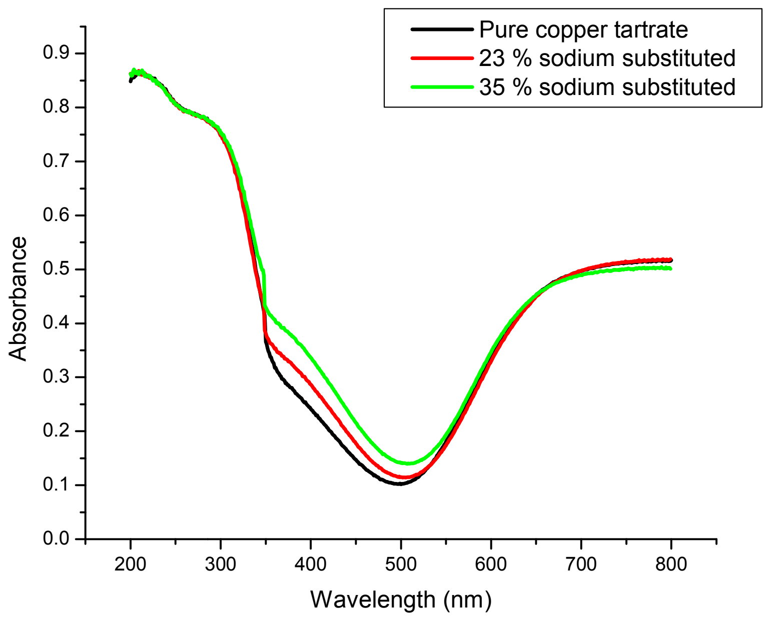


Figure 2: The UV-Vis absorption spectra of pure and modified copper tartrate crystals.

Crystal	Colour	Wavelength
Pure copper tartrate		
$CuC_4H_4O_6.3H_2O$	Bluish green	422-556
Modified copper tartrate		
$(Cu)_{0.77}(Na)_{0.23}C_4H_4O_6.3H_2O$	Light green	441-560
$(Cu)_{0.65}(Na)_{0.35}C_4H_4O_6.H_2O$	Dark green	459-553

Table 1: Colour and value of wavelength for pure and modified copper tartrate crystals

IV. Conclusion

From the above observations and discussion the following conclusions may be drawn:

1. Selective transparent wavelength range exhibited by both pure and modified copper tartrate in the visible region indicates the existence of colour cetres in these materials.
2. Copper tartrate in pure as well as in the modified form may emerge as new material with potential for device fabrication among the family of noble metal tartrate compounds.

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3. Modification of pure copper tartrate by Na^+ ions leads to a change in the colour of crystals and hence the range of wavelength emitted by the crystals.

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