

## Influence of addition of transition metal ions on the dielectric properties of Potassium hydrogen maleate single crystals.

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### ABSTRACT

Present work reports the dielectric properties of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{VO}^{2+}$  and  $\text{Cr}^{3+}$  doped potassium hydrogen maleate single crystals. The influence of addition of transition metal ions on the dielectric properties, like dielectric constant and dielectric loss of these crystals were discussed. The  $\text{Cr}^{3+}$  containing crystals exhibit lower dielectric loss at lower frequencies and all other have high dielectric losses. This indicates that the  $\text{Cr}^{3+}$  ions have a significant role in enhancing the optical quality of the crystal.

**Key words:** Dielectric constant, Dielectric loss, Potassium hydrogen maleate single crystals

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### Introduction

Potassium hydrogen maleate, hereafter KHM, is an acid salt of maleic acid. Earlier this has been reported to crystallize in centro- symmetric space group by Darlow and Cochran[1]. This has four molecules in unit cell. The dimensions of the unit cell are  $a= 4.578$ ,  $b= 7.791$  and  $c= 5.953$  Å. Recently Fleck and Bohaty [2] have attempted to redetermine the structure of KHM using X-ray diffraction and investigated the question of symmetry of maleate units . It has been suggested by them the space group of this crystal as assignment of spaces  $\text{Pbc2}_1$  rather than  $\text{Pbcm}$ . The studies on the crystals of alkali metal maleates have become a point of interest with this probable change of assignment of space group. In the past the spectral absorption properties of  $\text{Pr}^{3+}$  in Cadmium maleate dihydrate single crystals [3], absorption spectrum of  $\text{Ni}^{2+}$  in zinc maleate tetrahydrate single crystals [4] and absorption properties of  $\text{VO}^{2+}$  in cadmium maleate dihydrate single crystals [5] were reported. ESR studies on  $\text{Cu}^{2+}$  doped in potassium hydrogen maleate single crystals at 300 K were studied by Chandramouli [6] et al. Transport and thermal studies were reported by Reddy et al [7] for KHM crystals. The dielectric properties of pure KHM single crystals were reported by H. Kolodziej and L. Sobczyk [8]. Wilson [9] has made a systematic study of the symmetric hydrogen bond in KHM by variable pressure, neutron diffraction and plane wave DFT methods. There has been a considerable discussion over this symmetric hydrogen bond [10, 11] structure by neutron diffraction [12], vibrational spectra [13], Far IR spectra [14], inelastic neutron scattering spectroscopy [15] studies over KHM single crystals were reported earlier.

A search in the literature as well as in the databases has shown that no studies were reported on the dielectric properties of impurity doped KHM crystals. As a part of various other studies on alkali metal maleate single crystals, the dielectric measurements over transition doped KHM single crystals were carried out. The results of these studies were reported in this communication.

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## Experimental

Transition metal doped KHM single crystals were grown from the aqueous solution containing potassium hydrogen carbonate and maleic acid by slow evaporation method at room temperature.  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{VO}^{2+}$  and  $\text{Cr}^{3+}$  ions were introduced to an extent of 0.2 mol %, by the addition of solution of their respective carbonates/sulphates, using AnalaR grade reagents. The pure crystals are transparent, platy with 001 phase and the doped crystals are platy and coloured. The colours of these crystals were as expected for that of the transition metal ions and in correlation with the reported crystals in the literature.

Good quality KHM crystals were grown from aqueous solution within a period of two weeks. The platy crystals were optically polished and used for present study. The dielectric constant measurements on doped KHM crystals were carried out using Hioki Hitester 3532-50 LCR meter with conventional two terminal sample holder at room temperature. From the capacitance data, the dielectric constant is calculated using equation (1.1).

$$\epsilon' = \frac{C t}{A \epsilon_0} \dots\dots\dots 1.1$$

where 'C' is capacitance, 't' is the thickness, ' $\epsilon_0$ ' permittivity of the free space ( $8.85 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ ) and 'A' the area of the sample.. The loss tangent or dissipation factor is taken from the data.

The a.c. conductivity ( $\sigma_{ac}$ ) is calculated using the relation equation (1.2)

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta \dots\dots\dots 1.2$$

$\omega$  is the angular frequency. The observations are made in the frequency range 100Hz to 6 MHz at room temperature.

## Results and Discussion

The dielectric measurements were performed on pure and transition metal ion doped KHM crystals. The dielectric constant and dielectric loss at frequency 1 MHz at room temperature for all the crystals was presented in table 1 for comparison.

**Table 1** Comparison of dielectric properties at 1MHz and room temperature.

Crystal	$\epsilon'$	$\tan \delta$
KHM : $\text{Ni}^{2+}$	59.26	0.136
KHM : $\text{Cr}^{3+}$	63.89	0.122
KHM : $\text{Co}^{2+}$	123.21	0.134
KHM : $\text{VO}^{2+}$	192.42	0.113
KHM : $\text{Cu}^{2+}$	269.81	0.123

Fig 1 shows the variation of dielectric constant as function of frequency for the transition metal doped KHM single crystals. It was observed that at low frequencies the dielectric constant decreases rapidly with frequency and attains almost a constant value at high frequencies. Further, there was no significant difference in the overall variation of dielectric constant with addition of transition metals ion. The higher dielectric constant value at the low frequency for all the KHM crystals under study can be attributed to the presence of higher space charge polarization [17, 18]. In accordance with Miller rule, the lower values of dielectric constant at higher frequencies are generally expected. The results indicate that all the crystals under study exhibit this behaviour. The  $\text{Cu}^{2+}$  doped KHM has a high dielectric constant when compared to other crystals under study. The data reveals that  $\text{Cr}^{3+}$  doped KHM crystal has a low dielectric constant compared to other crystals. The variation in the dielectric constant with frequency is almost similar with different dopants but with different magnitudes.

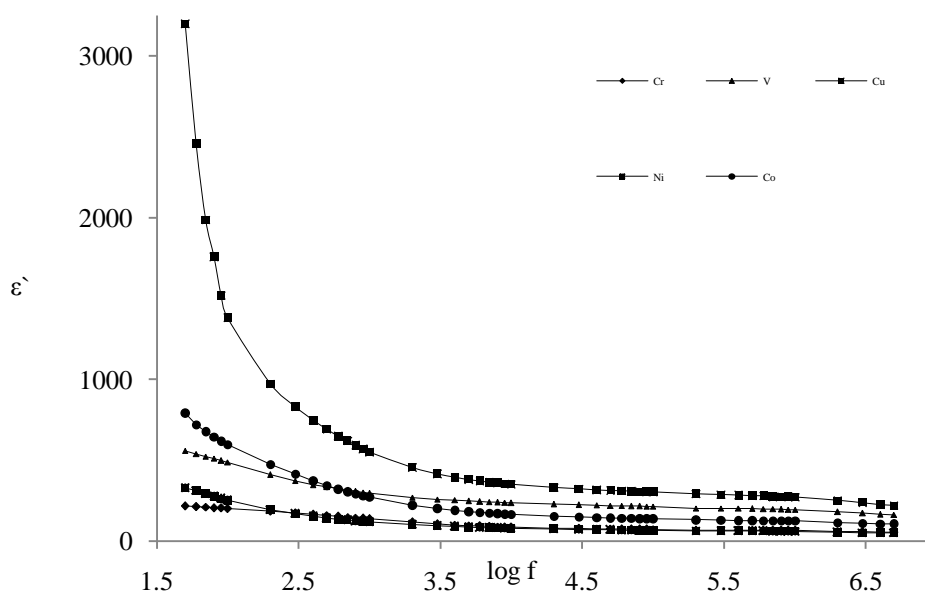


Fig. 1. Variation of dielectric constant with frequency for transition metal doped KHM single crystals

Fig 2 shows the variation of dielectric loss with frequency for the crystals under study. The dielectric loss decreases with increase in the frequency in all the crystals except in the  $\text{Cr}^{3+}$  doped KHM. The dielectric loss in  $\text{Cr}^{3+}$  doped KHM crystal increases initially and reaches a maximum and then decreases. At higher frequencies the dielectric loss was almost constant and also independent of transition metal ion doped into the crystals. The low dielectric loss at lower frequencies is an indication of the optical quality and the defect formation. The  $\text{Cr}^{3+}$  containing KHM exhibits lower dielectric loss at lower frequencies and all others have high dielectric losses at these frequencies. This indicates that the  $\text{Cr}^{3+}$  ions have a significant role in enhancing the optical quality of the crystal.  $\text{Cr}^{3+}$  ions in the crystal lattice decreases the number of defects in the crystals as a low dielectric loss is the indicator of fewer defects in the crystals.

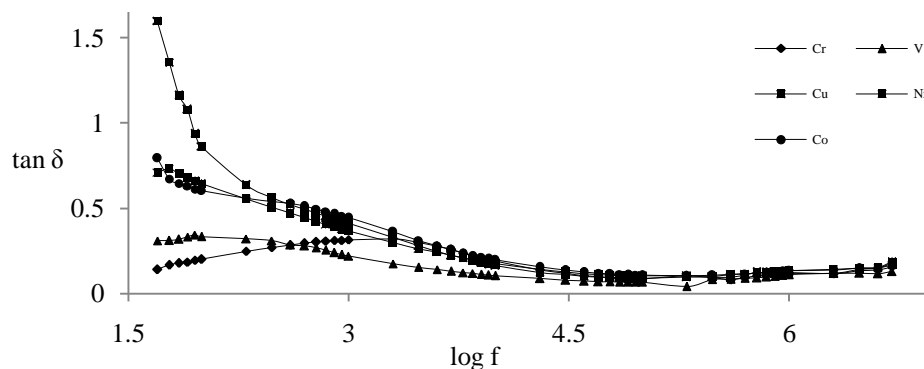


Fig 2: Variation of  $\tan \delta$  with frequency for transition metal doped KHM single crystals

Fig 3 shows the variation of ac conductivity with frequency for the crystals under study. This indicates that as the frequency of the applied field increases, the a.c. conductivity remains constant in the low frequency range and increases rapidly at high frequencies. The increased conductivity at higher frequencies can be attributed to the contribution of polarons. It can be noticed that the  $\text{Cr}^{3+}$  doped KHM single crystals exhibits very low a.c. conductivity at higher frequencies when compared to other crystals under study. The results of a.c. conductivity studies suggest that the conductivity mechanism in this crystal was identical in all the KHM single crystal and not significantly different from one other.

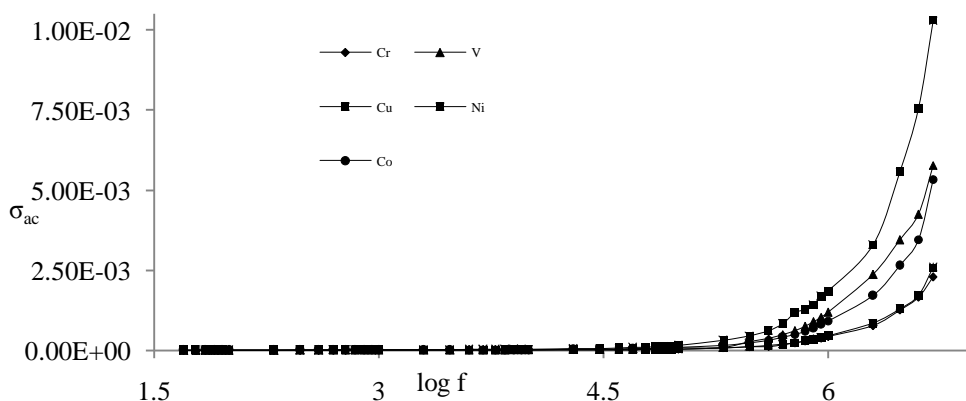


Fig. 3. Variation of a.c. conductivity with frequency for transition metal doped KHM single crystals

## 4 Conclusions

Good quality KHM single crystal doped with transition metal ions were grown successfully by slow evaporation technique at room temperature. Dielectric properties of these single crystals were measured and reported for the first time. The incorporation of transition metal ions into the KHM crystal lattice may lead to the change in the position of atoms in the hydrogen bond due to their difference in radii a shift or change in the position in the case of either potassium or maleate ions can also be expressed. It is generally expected whenever a transition metal ion enter the lattice it may lead a probable removal of 2, 3 or 4 hydrogen atoms to affect the charge compensation. However, such a removal of H atom cannot be established in these studies. The overall dielectric

behaviour of the single crystals were not different from one another indicating that the role played by the dopant ions could not change the overall mechanism but individually each ion is influencing the mechanism in different magnitudes. All the crystals under the study have lower values of dielectric constant at higher frequencies. This is a suitable parameter for enhancing the SHG coefficient. The characteristics of low dielectric loss at high frequencies for these KHM single crystals suggests that these crystals possess improved optical quality with lesser defects and this parameter plays important role for the construction of devices.

## References

- [1] S.F. Darlow and W. Cochran, *Acta Cryst.*, 14, [1961] 1250
- [2] Michel Fleck and Ladislav Bohaty, *Z. Naturforsch.*, 64b, [2009] 517
- [3] M.V. Ramana, *Crys Res Tech.*, 27, [1992] 3 K57
- [4] M.V. Ramana, *Crys Res Tech.*, 30, [1995] 5 K46
- [5] K. Ravindra Babu and M.V. Ramana, *Cryst Res Tech.*, 26, [1991] 9 K185
- [6] V. Chandra Mouli and G.S. Sastry, *J. Mol Struct.*, 82, [1982] 251
- [7] A.D. Reddy, S.G. Satyanayanan and G.S. Sastry, *Pramana*, 22, [1984] 49
- [8] H. Kolodziej and L. Sobczyk, *Acta Phys PolA*, 39, [1971] 59
- [9] C. Wilson, *Chem Phys Lett*, 381, [2003] 102
- [10] F. Fillaux, A. Cousson and J. Tomkinson, *Chem Phys Lett*, 399, [2004] 289
- [11] C. Wilson, L. Thomas and C. Morrison, *Chem Phys Lett*, 399, [2004] 292
- [12] S.W. Peterson and A. Henri Levy, *Chem Phys*, 29, [1958] 948
- [13] F. Avbelj, B. Orel, M. Klanjek and D. Hadi, *Spectrochim Acta A*, 41 [1985] 75
- [14] H. Zelsmann, Z. Mielke and M. Ilczyszyn, *Spectrochim Acta A*, 44 [1988] 705
- [15] J. Tomkinson, *Chem Phys*, 64, [1982] 151
- [16] M. Meena and C.K. Mahadevan, *Cryst Res Tech*, 43, 2 [2008] 166
- [17] B. Narsimha, R.N. Choudary and K.V. Rao, *Mater Sci*, 23, [1988] 1416
- [18] S.M. Dharma Prakash and P. Mohan Rao, *Journ Mater Sci Lett*, 8 [1989] 1167