OPTICAL PROPERTIES OF GUANIDINIUM ALUMINIUM SULPHATE HEXAHYDRATE

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ABSTRACT: Single crystals of Guanidinium Aluminium Sulphate Hexahydrate (GASH) were obtained.The crystallographic and optical properties of this material are given.Transmission of monochromatic light was measured for both pure GASH and the compound doped with Cr atoms.Using these data the value of the energy gap for pure GASH was calculated and also the appearance of new energy levels in the forbidden energy zone when GASH was doped with Cr was discussed.Far infrared reflectivity was measured for pure GASH and the experimental results were numerically analysed.The values of some optical parameters were calculated.

1.INTRODUCTION

Gvanidinium Aluminium Sulphate Hexahydrate (GASH) with the formula $/C(NH_2)_3/Al(SO_4)_2{}^6H_2O$ is a ferroelectric substance whose Curie temperature is 473K.

GASH has a hexagonal structure with lattice parameters: $a=11.738\pm0.002\mathring{A}$ and $c=8.951\pm0.002\mathring{A}$ /1/,/2/ and the space group P31m (C_{3v}^2).It has three molecules per unit cell.

In this work,as far as we know,the optical properties of pure GASH have been studied for the first time in both the visible and far infrared ranges.The effect of doping with Cr was also examined.

2.EXPERIMENTAL

Single crystals of pure GASH and GASH doped with Cr were made from a solution by a standard technique.Using an X-ray diffractometer only Bragg´s diffractions corresponding to the following plane were observed:(001),(002),(003).Pure GASH was colourless and transparent like glass,while GASH doped with chromium had a pale violet colour.The transmission of monochromatic light was measured in these samples in the visible range.Visible transmission spectra of two single crystal GASH specimens are given in Figures 1a and 1b.The former is for pure GASH and the latter for GASH doped with chromium.

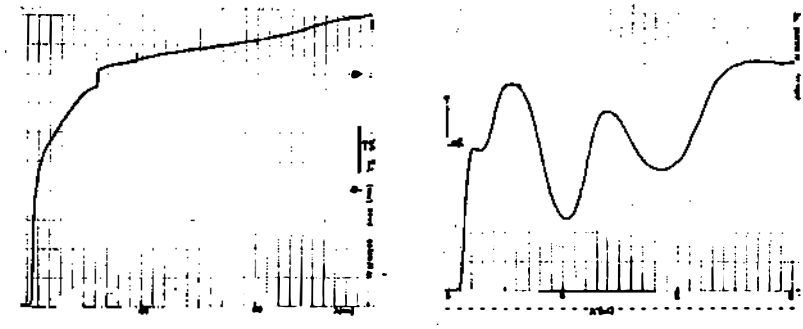

Figure 1.Transmission spectra in the visible range for pure GASH (a) and GASH doped with Cr (b).

Pure GASH was very transparent and had an almost constant transmission in the whole visible range which decreased quickly in the range of the absorption edge.GASH doped with chromium has three rather wide absorbing energy ranges at about 2.58 eV,3.04 eV and 4.84 eV below the bottom of the conduction zone.

Far infrared reflectivity measurements using polarized light were done with a Fourier spectrometer (Beckmann FS 720).The variation of near normal incidence reflectivity for pure GASH is given in Figures 2a and 2b for E//c and E$\perp$c,respectively.The experimental data are represented by squares,while the solid lines were calculated using oscillator parameters which were obtained by numerical analysis carried out with the aid of a fitting procedure according to the Gervais /3/ four parameter model.

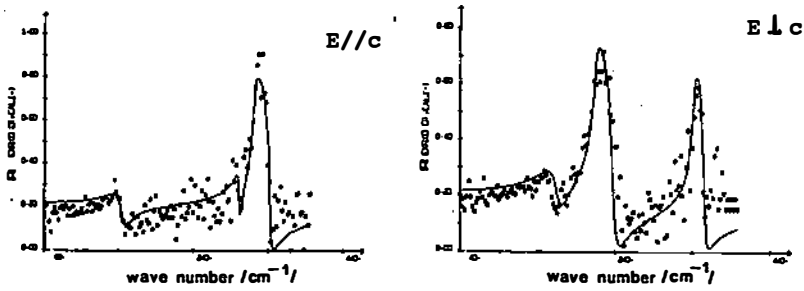

Figure 2. Experimental far infrared reflectivity data versus wavenumber represented as squares for E//c (a) and E⊥c (b). The solid lines were calculated using the oscillator parameters given in Table 1.

The values of tranversal (ω_{TO}) and longitudinal (ω_{LO}) optical modes and their damping factors (γ_{TO} and γ_{LO}) for six oscillators are given in Table 1,together with the values of the high frequency dielectric constants (ε_∞).

Table 1

	$\omega_{TO}(cm^{-1})$	$\gamma_{TO}(cm^{-1})$	ω_{TO} (cm^{-1})	$\gamma_{LO}(cm^{-1})$	ε_∞
	141	18	147	13	
E//c	301	5.5	303	2.5	6
	321	2	343	3	
	161	24	166	17	
E⊥c	214	5	242	9	5
	341	6	356	6	

Table 1.Optical parameters used to fit infared reflectivity spectra.Frequencies and damping factors are expressed in units of cm^{-1}.

3.DISCUSSION

To obtain a complete picture about the number of possible infrared and far infrared active modes we have done a factor group analysis for GASH.Taking into account that its unit cell has three molecules and using the known Wyckoff´s sites /4/ we have calculated the number of Raman and infrared active modes in the Brillouin zone using Adams-Newton tables /5/.

$$\Gamma = 46A_1 + 35A_2 + 81E$$

The number of accoustical modes is N=3 and they have the symmetry (A_1+E).In that case we calculated that there are $46A_1$+81E Raman active modes,45 infrared active modes for E//c and 80 infrared active double degenerated modes for E⊥c

If we compare the number of infrared active modes that we observed with the calculated values,it is very obvious that there are big differencies.In addition to obtaining far infrared reflectivity data we have done similar measurements in the infrared range using polarized light.In the infrared range,between 2000 and 400cm^{-1} we observed another 7 oscillators,three for E⊥c and four for E//c.That means that 6 oscillators were experimentally observed for E⊥c and seven oscillators for E//c.

The number of calculated active modes is not correct because for three GASH molecules per unit cell (with 39 atoms per molecule) there should be 39x3x3=351 optical phonons.For the Wyckoff sites of GASH accepted in the literature /4/ there are only 46 + 35 + 2x81 =243 optical phonons.We would like to point out that this disagreement with the calculated number of optical phonons means that Wyckoff's sites are not correctly obtained so some further investigations should be done concerning that problem.

Using the obtained transmission diagrams,given in Figure 1a and 1b we calculated the energy gap of pure GASH to be 5.64eV.The violet colour of GASH doped with chromium is the consequence of the energy levels at about 3eV,which were formed by this dopant.

4. REFERENCES

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