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Structural, thermal and electrical characterisation of ferroelectric single crystal: Guanidinium Cobalt Sulphate Heptahydrate

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Abstract : Semi organic single crystal of guanidinium cobalt sulphateheptahydratewas grown from its aqueous solution by slow evaporation solution growth technique. Powder X- ray diffraction analysis (PXRD) was carried out to confirm the formation of the crystalline compound. The functional groups present in the crystal were identified by FTIR spectroscopic analysis.Thermo gravimetric and differential thermo gravimetric analyses (TG-DTG) were performed to analyse the thermal behaviour of the grown crystal. The dielectric constant and dielectric loss of the grown crystal were studied as a function of frequency of the applied field. The ferroelectric nature of the grown crystal was analysed by P-E hysteresis loop.

Key words : Slow evaporation, PXRD, TG-DTG, P-E hysteresis loop.

Introduction

The growth of linear and nonlinear optical single crystals gains momentum for the past few decades. There has been a growing interest in the field of crystal growth due to the increasing demand of the crystal materials for modern technological applications in the field of semiconductors, solid state lasers, nonlinear optics, piezoelectric, photosensitive materials and crystalline thin films for microelectronics and computer industries. Hence the single crystal growth and its characterisation towards device fabrication are important in the academic as well as applied research. Guanidinium compounds play a major role in the field of non linear optical crystal growth. The guanidinium ion $[C\ (NH_2)_3]^+$ is an important functional group present in the amino acid and also the basic constituent of many biologically active molecule [1]. It is a strong base which reacts with most organic acid resulting in the formation of guanidinium species. A large number of guanidinium based linear and nonlinear optical single crystals were reported in the literature. The crystal structure, vibrational spectroscopic studies and ferroelectric properties of some guanidinum metal sulphates have been reported in the literature [2-3]. Guanidiniumaluminiumsulphatehexahydrate and some of its isomorphous materials were

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reported to be ferroelectric material and its dielectric properties were also discussed in detail [4]. Many guanidinuim based nonlinear optical crystals were reported from our lab[5-7]. With our continuing interest on guanidinium compound, in this paper we report the growth and characterisation of the guanidinuim compound namely guanidinium cobaltsulphateheptahydrate [GuCoS].

Experimental

Material synthesis and crystal growth

Theguanidinium cobalt sulphate was synthesised using AR grade guanidinium carbonate, concentrated sulphuric acid and cobalt sulphateheptahydrate. The chemicals were used without further purification. The reagents were taken in the equimolar ratio and dissolved in distilled water at room temperature. The solution was stirred using magnetic stirrer for more than five hours to ensure the homogenous concentration. Once the solution reached the saturation condition it was filtered using Whatmann filter paper and kept for slow evaporation of the solvent in a clean atmosphere. After a period of six days the compound found to crystallise at the bottom of the container. The following equation explains the scheme of synthesis.

$$[C\,(NH_2)_3]_2CO_3 + H_2SO_4 \rightarrow [C\,(NH_2)_3]_2\,SO_4 + H_2O + CO_2\uparrow$$

$$[C\,(NH_2)_3]_2\,SO_4 + CoSO_4.7H_2O \rightarrow Co[C\,(NH_2)_3]_2\,(SO_4)_2.\,7H_2O.$$

The purity of the synthesized compound was further improved by repeated recrystalisation with the same solvent and used for the growth of the single crystals. A saturated solution was prepared from the recrystallisedguanidinium cobalt sulphate salt and allowed to evaporate in a dust free atmosphere. After a period of eleven days red coloured crystal of guanidinium cobalt sulphate was harvested and is shown in the Fig. 1.

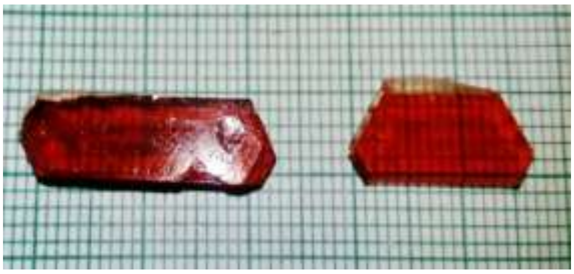

Fig. 1 Photograph of GuCoS crystal.

Results and discussion

Powder X-ray diffraction analysis

The powder X- ray diffraction pattern of the crystal is important in determining the crystallanity and phase purity of the grown crystal. The powder X-ray diffraction analysis of the grown crystal was recorded using RICH SIEFERT powder X-ray diffractometer with Cu Kα (λ=1.5406Å) radiation. Grown crystals were ground using agate mortar and pestle and subjected to powder X-ray diffraction analysis. The sample was scanned in the range 10º-70º in steps of 0.04º per second. The powder X-ray diffraction pattern of the grown crystal is shown in the Fig. 2.The intense and sharp peaks in the diffractogram indicate the crystalline perfection of the grown crystals.

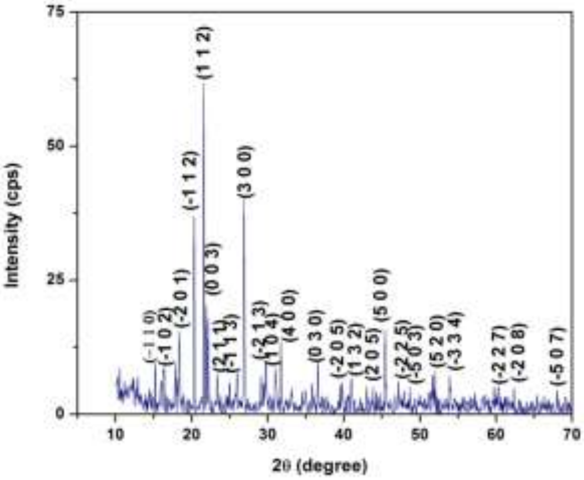

Fig.2 Powder X-ray diffraction pattern of GuCoS crystalline sample

The experimental two theta values obtained from the powder X-ray diffractogram was used for indexing the powder pattern. The indexing of the peaks and the evaluation of the lattice cell parameter were carried out using the software PROSZKI version 2.4. It was found that the grown crystal GuCoS belongs to monoclinic crystal system and the space group was found to be $P2_1/c$ which is a centrosymmetric crystal. The cell parameters of the crystal are, a = 10.076 Å, b= 7.389 Å, c= 12.138 Å, α=90°, β=95.775°, γ=90° &V=899.137Å^3.The calculated lattice cell parameters agree well with the reported values [2].

FTIR spectral analysis

FTIR is an important technique for the identification of the various functional groups present in the grown crystal. The FTIR spectrum was recorded in the range between 450 – 4000cm^{-1}using Perkin Elmer spectrum one spectrophotometer.The observed spectral bands are assigned in terms of the fundamental modes of vibration of the guanidinium ion $[C(NH_2)_3]^+$,sulphate ion(SO_4^{2-})and water molecules [3]. The recorded FTIR spectrumof GuCoS is shown in Fig. 3.

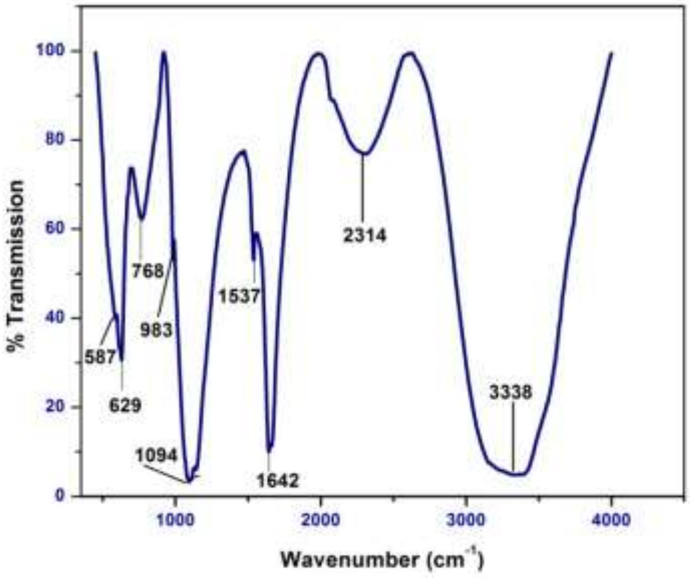

Fig. 3 FTIR spectrum of GuCoS crystalline sample

Vibrations of Guanidinuim ions

The vibrational modes of guanidinium ions can be assigned by considering the C-N bonds as a group frequency of CN_3 and the N-H bonds with another group frequency of NH_2. In the IR spectrum of the title compound,the presence of a sharp strong band at 1642cm^{-1}and a weak band at 768 cm^{-1}are due to asymmetric stretching vibrations of CN_3 group. The band at 1537cm^{-1} is assigned to the bending of NH_2 group.

Vibrations of the sulphate group

The sulphate group (SO_4^{2-})in its free ion state usually has four fundamental modes of vibration. The modes are the non degenerate symmetric stretching mode (ν_1), the doubly degenerate symmetric bendingmode (ν_2), the triply degenerate asymmetric stretching mode (ν_3), and the triply degenerate asymmetric bending mode (ν_4) with the wave numbers 981 cm^{-1}, 451cm^{-1},1108 cm^{-1} and 613 cm^{-1} respectively. Among the four different modes of vibration, only (ν_3) and (ν_4) are IR active [3]. The non degenerate symmetric stretching mode (ν_1) is also found to be active in GuCoS and appears as a weak band at 983 cm^{-1}. The (ν_3) mode of sulphate ion has a strong bandat 1094 cm^{-1}in the FTIR spectrum. The asymmetric bending mode (ν_4) appears at 587 cm^{-1} and 629 cm^{-1} in the IR spectrum.

Vibrations of water molecule

A water molecule has three fundamental vibrational modes: (ν_1) at 3652 cm^{-1}, (ν_2) at 1595 cm^{-1} and (ν_3) at 3756 cm^{-1}. The IR spectrum of GuCoS contains a strong band at 1537 cm^{-1}which is assigned to the (ν_2) vibrationalmodes of water molecule.The broad band at 3338 cm^{-1}indicates the presence of (ν_1) vibrational modes of water molecules in the sample. The vibrational band assignments of FTIR spectrum of the grown crystal was found to be in good agreement with that of the values reported in the literature [3]. The experimental vibrational frequencies of GuCoS are presented in Table 1.

Table 1 Vibrational band assignments of GuCoS

Wavenumber (cm^{-1})	**Band Assignment**
587 m	ν_4 SO_4
629 m	ν_4 SO_4
768 w	$\nu_{as}CN_3$
983 m	ν_1 SO_4
1094 s	ν_3SO_4
1537 w	ν_2 H_2O
1642 s	$\nu_{as}CN_3$
3338 s	ν_1 H_2O

w- weak; m- medium; s- strong.

ν_s- symmetric stretching; ν_{as}- asymmetric stretching

Thermal studies

Thermal decomposition is the process in which a substance decomposes due to the application of heat. This phenomenon is common to most organic substances and occurs in many inorganic substances as well.Certain substances can undergo multistage decomposition reaction each at a different temperature.The thermal stability of GuCoS was studied by thermogravimetric (TG) and differential thermogravimetric analyses (DTG). Using TG-DTG curve the decomposition temperature and the percentage mass loss of each stage can be easily determined. The GuCoS sample initially weighing 6.985 mg was heated in an alumina crucible in the nitrogen atmosphere at the flow rate of 20 mL per minute. The sample was heated in the temperature range between 20 °C and 1400 °C at the rate of 10 °C per minute and the resultant thermogram is shown in Fig. 4. A careful examination of the TG curve elucidates the occurrence of eight stage weight loss pattern and it is also evident that the GuCoS compound is stable upto87°C after that the sample undergoes appreciable weight loss. The first stage weight loss occurring at 87°C with the elimination of 7.48 % of the initial mass which may probably due to the evaporation of water molecule in the sample. The DTG spectrum shows the corresponding sharp peak at the same temperature range. The second stage weight loss was observed between 87°C and 122°C with a weight loss of about 16.54 % which may probably due to the decomposition of the guanidinium compound with the release of ammonia. The decomposition process was carried out upto 1400 °C and the residual mass was stabilised at 17.87 % of the initial mass.

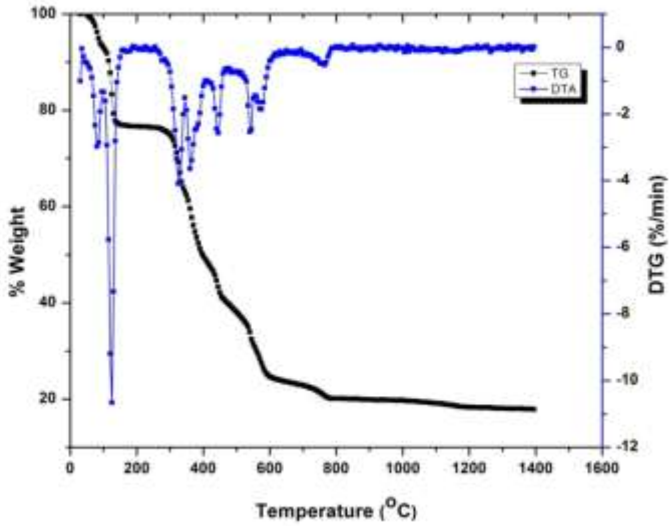

Fig 4. TG-DTG curve of GuCoS crystalline sample

From the thermogram it is clear that theGuCoS crystal can be exploited for practical applications upto87ºC.The sharpness of DTG peaks is attributed to the good crystalline nature of the grown crystal.

Dielectric Study

The dielectric properties of the optical materials are related with the electro - optic properties. The dielectric constant (relative permittivity of the medium) is a measure of the degree to which a medium can resist the flow of charge. It is the ratio of the electric displacement (D) to the electric field (E). The single crystal of GuCoS with the dimension 6.93mmx10.47 mmx4.17 mm was used for the dielectric measurement using HIOKI 3532 LCR HITESTER in the frequency range between 50 Hz and 5 MHz. The measurements were carried out in the range between the room temperature and 60 °C. The crystal having silver coating on the opposite faces is placed between the two copper electrodes to form a parallel plate capacitor. The dielectric constant of the material of the crystal was calculated using the relation [8]:

$$\boldsymbol{\varepsilon}_{\mathrm{r}}= \frac{\boldsymbol{Ct}}{\boldsymbol{A\varepsilon_0}}(1)$$

where C is the capacitance, A is the area of cross section, $\epsilon_0$is the permittivity of free space and t is the thickness of the crystal. The variation of dielectric constant as a function of frequency at different temperatures is shown in the Fig. 5.

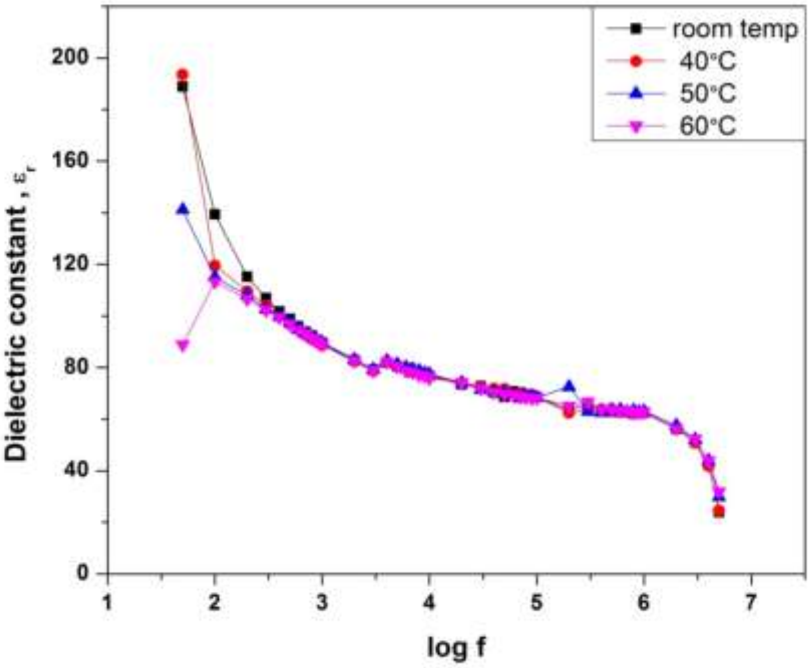

Fig 5.Variation of dielectric constant with frequency at different temperatures

From the graph it is clear that the dielectric constant is high at lower frequency and starts decreasing gradually for higher frequencies. The dependence of dielectric constant with frequency shows a similar trend for all temperatures. The electronic exchange of the number of ions in the crystal gives local displacement of electron in the direction of applied field which in turn give rise to polarisation. The high value of dielectric constant in the low frequency region may be due to the contribution from all four polarisations namely: electronic, ionic, orientation and space charge polarisations. As the frequency of the applied field increases and a point will be reached where the space charge cannot sustain and hence the dielectric constant starts to decrease.Hence the gradual decrease of dielectric constant at higher frequencies is attributed to the loss of significance of all the four polarisations [9].

The variation of dielectric loss (tan δ) with frequency at different temperatures is shown in the Fig. 6. From the curves it is clear that the dielectric loss values are high at lower frequencies and starts decreasing gradually for higher frequency.Hence the gradual decreases of dielectric constant as well as the dielectric loss at higher frequency suggest that the crystal possesses enhanced optical quality with lesser defects which is an important parameter of the nonlinear optical materialsin their high speed electro-optic modulation [10].

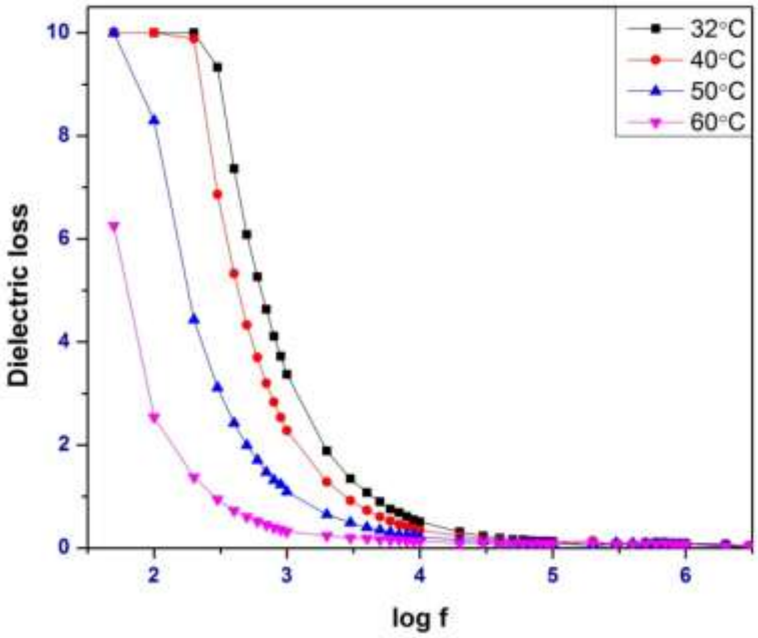

Fig 6 Variation of dielectric loss with frequency at different temperature

Also the low values of dielectric constant and dielectric loss of the grown GuCoS crystal at higher frequencies suggest that the crystal can be exploited for ferroelectric and electro optic device applications.

P-E Hysteresis analysis

Ferroelectric materials are important for the study of phase transitions, electron-phonon interactions and other optical and electrical phenomena in condensed matter. The nonlinear dependence of polarisation (P) on the electric field (E) leads to a hysteresis loop, which is one of the important characteristics of ferroelectric materials. Ferroelectric domains present in the material possess spontaneous polarisation and the magnitude and direction of this spontaneous polarisation can be reversed by the application of a strong external electric field. An important characteristic of ferroelectrics is the hysteresis loop in the polarisation versus electric field curve.

The polarisation and electric field (P-E) hysteresis curve was traced forGuCoS crystal using Radiant – precision 4 kVHVI loop tracer. A good quality crystal of size 5 mm x 5 mm x 1mm was used for this analysis. The opposite faces of the crystal were coated with conductive silver paste for electrical contact. The obtained P – E hysteresis curve is shown in Fig. 7.

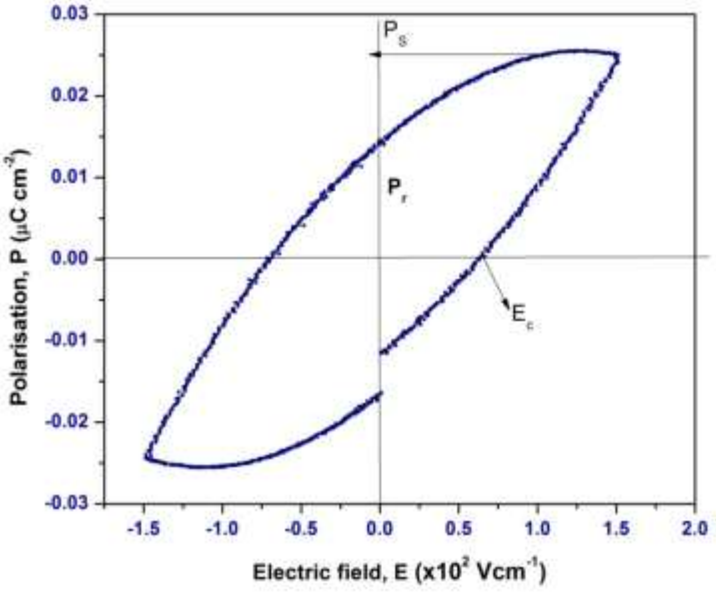

Fig.7 P –E Hysteresis curve of GuCoS crystal

From the hysteresis curve the value of remnant polarisationP_r is found to be 0.014μC/ cm^2. An extrapolation of the saturation value to zero field gives the magnitude of the spontaneous polarisation P_s. The spontaneous electric polarisation P_s at room temperature is found to be 0.025μC/ cm^2, whereas for guanidiniumaluminiumsulphatehexahydrate (GASH) the value of P_s was reported as 0.35 μC/ cm^2 [4]. The value of coercive field E_c is found to be 65 V/ cm. Since the crystal exhibits saturation P –E hysteresis curve it could be exploited for ferroelectric capacitor, radio and communication filter and non volatile memory applications.

Conclusion

A potential semi organic ferroelectric single crystal of guanidiniumcobalt sulphateheptahydrate [GuCoS] was grown from its aqueous solution by slow evaporation solution growth technique. The formation of the compound was confirmed by powder X-ray diffraction analysis. From the TG-DTG curve it is evident that the material is stable up to 87°C. The variation of dielectric constant with applied field frequency and temperature was analysed and it is found that the crystal exhibits low dielectric loss which is an important property for device application. The grown crystal exhibits P-E hysteresis loop and the value of the saturation polarisation is found to be 0.025μC/ cm^2.

References

1. Sension R.J.,Hudson B., Callis P.R., Resonance Raman studies of Guanidinium and substituted Gu ions, J.Phys.Chem., 1990,94,4015-4025.
2. Fleck M., Bohaty L., Tilmanns E., Structural charecterisation of M^{II}guanidiniumsulphate hydrates, Solid State Sci., 2004, 6, 469-477.
3. JuanidBushri M., Antony C.J., Michel Fleck., Vibrational spectroscopic studies of Guanidinium metal (M^{II})sulphatehexahydrates, Solid State Commun., 2007,143 ,348-352.
4. Matthais B T.,Berkeley Heights N J., Ferroelectric devices, US Patent office 1959, Aug.25.
5. Sivasankar V., Siddheswaran R., Murugakoothan P., Synthesis, growth, structural, optical, and thermal properties of a new semi organic nonlinear optical guanidinium perchlorate single crystal, Mater.Chem.Phys., 2011, 130, 323-326.
6. Arumanayagam T., Murugakoothan P., Studies on optical and mechanical properties of new organic NLO crystal: Guanidinium 4-aminobenzoate, Mater. Lett., 2011, 65, 2748-2750.

7. Suvitha A., Murugakoothan P., Synthesis,growth, structural, spectroscopic, and optical properties of a semiorganic NLO crystal: Zinc guanidinium phosphate,Spectrochim. Acta A., 2012,86, 266-270.
8. Arjunan S., Bhaskaran A., Mohan Kumar R., Jayavel R., Effect of rare-earth dopants on the growth and structural, optical, electrical andmechanical properties of l-arginine phosphate single crystals,J.Alloy. Comp., 2010, 506 ,784-787.
9. PrasadN.V., Prasad G.,Bhimasankaran T., Suryanarayana S.V.,Kuamar G.S., Growth and charecterisation of L- Alanine sodium sulphate anhydrous single crystals,Indian J. Pure Appl.Phys., 1996, 34, 639.
10. Thomas P C., Lanka bhushankumar., Anuradha A., Aruna A., Joseph G P., Sagayaraj P., Growth and characterisation of nonlinear optical single crystals of L –Arginine diiodate, J Cryst.Growth, 2006, 290, 560-564.

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