Growth and Characterization of Tetrathiourea Potassium Iodide Doped KCL Crystal

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Abstract - Single crystals of tetrathiourea pottasium iodide (TTPI) be developed by slow evaporation method. Single crystal X-ray analysis investigation demonstrates that TTPI takes crystal system framework. The title compound was further portrayed by UV-Vis-NIR examine demonstrates that the single crystal is straightforward in the specific wavelength range and TG/DTA examination. Dielectrics studies examine on the developed grown crystal determine the dielectric steady and dielectric misfortune as for frequency.

Key Words: Crystal growth, Photo Luminescence and Dielectric.

I. INTRODUCTION

However, their often in-adequate transparency, poor optical quality, lack of stoutness, low laser damage verge and incapability to grow to larger size have impeded the use of single crystals of organic materials in practical applications in devices. Hence materials scientists focused their attention on novel materials in order to satisfy the present day technological needs. In the recent past a new class of materials have been developed i.e. semiorganic crystals. Semiorganic crystals have extensive nonlinearity, high resistance, too large induced damage, low angular sensitivity and good mechanical hardness (Xing *et al.*, 1987; Verko, 1990; Warren, 1990; Kotler *et al.*, 1992).

Recently, the nonlinear optical (NLO) properties of certain results of thiourea (Jiang et al., 1985; Venkataraman et al., 1995; Hou et al., 1993) have pulled in extraordinary importance, on the grounds that these metal-organic materials have the potential for combining high optical nonlinearity and the compound adaptability of organics with the physical roughness of inorganics. The thiourea atom is a attractive inorganic grid modifier because of its expansive dipole moment and its capacity to shape a broad system of hydrogen bonds. The centrosymmetric thiourea particle, when joined with inorganic salts yields noncentrosymmetric molecules, which has nonlinear optical properties.

Metal complexes of thiourea, regularly called semiorganics, incorporate the upside of both organic and inorganic piece of the complex. A variety of crystals has been developed by several groups (Venkataraman et al., 1997; Bhat and Dharmaprakash, 1998; Anie Roshan et al., 2001; Rajasekaran et al., 2001). In the present examination, thiourea is joined with potassium chloride to frame another semiorganic nonlinear optical material. In this study, we report the growth of single crystals of potassium thiourea chloride by slow evaporation technique and its categorization.

The non-linear optical properties of some complexes of thiourea have involved significant interest over the most recent couple of years, because both organic and inorganic moleculs in it contribute exclusively to the development of second harmonic generation. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds.

Thiourea, which is centro symmetric, yields excellent non-centro symmetric materials when it is incorporated into the respective inorganic salts. Based on the above given information, synthesis and growth of semiorganic nonlinear optical material of tetra thiourea potassium iodide (TTPI) was prepared. The grown crystal was studied to various characterization techniques such as single crystal XRD, powder XRD, FTIR, UV-Vis-NIR spectra, thermal, dielectric studies and hardness test, respectively.

II. MATERIAL SYNTHESIS AND CRYSTAL GROWTH

Single crystal of Tetra Thiourea Potassium Iodide (TTPI) Doped KCl was synthesised by dissolving of thiourea and potassium Iodide in triple distilled water in a molar ratio 4:1. Potassium chloride (KCl) react as an additive is added into thiourea potassium Iodide solution in a small amount (1M%) slow evaporation method at room temperature to get a new crystal. Raw materials used in the growth process were analytical reagent grade (E MERCK). Since thiourea has synchronization ability to form altered phases of metal-thiourea complexes, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases.

The solution was thoroughly stirred for 7hrs using magnetic stirrer in room temperature. The prepared solution was filtered in a whatman filter paper. The beaker was covered with transparent paper to avoid dust inclusion and kept at

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room temperature. The purity of TTPI doped KCl crystals were done by recrystallization method. TTPI crystals were grown form aqueous solution by slow evaporation techniques. TTPI was synthesized according to the following reaction:

$$KI + 4[CS(NH2)2] \rightarrow K[CS(NH2)2]4I$$

The synthesized TTPI crystal was purified by consecutive recrystallization processes. Good optically transparent KCl doped TTK Iodide crystals have been crystallized with well defined faces in a period of 35 days. Due to the doping of the impurities on the crystals, remarkable changes in the physical properties were obtained (Fig.1).

III. RESULTS AND DISCUSSIONS

1.3.1 Powder XRD analysis

The synthesized crystals have been analyzed by characterization techniques. Single crystal of TTPI was definite by single crystal XRD analysis using ENRAF NONIUS CAD4 diffractometer with CuKα Radiation (λ =1.5406). The powdered sample was scanned over the range of 10 to 70 degrees. The peaks in the diffractogram were indexed to analyses. The XRD pattern of the grown crystal of tetra thiourea potassium lodide doped kcl as shown in the Fig. 2. In the crystalline material have been investigated, well defined peaks will be observed (Renganayaki, 2011; Farhana Khanum and Jiban Podder, 2011). The availability of good intensity and sharp peaks confirm the crystalline nature of the grown crystals.

1.3.2 Fourier Transform Infrared analysis

Infrared spectroscopy is productively used to establish the molecular structure and the recognition of the functional groups in the synthesized compound (Venkattaramanan *et al.*, 1997; Yang *et al.*, 2013). The powdered specimen of TTPI was subjected to FTIR analysis by using PERKIN ELMER RXl Fourier Transform Infrared spectrophotometer. The FTIR analysis of TTPI was carried out, using KBr pellet procedure in the region 4000 to 400 cm^{-1}. The recorded FTIR spectrum of TTPI is shown in Fig. 3, there are two potential by which the coordination of potassium with thiourea may occur whichever through nitrogen or through sulfur of thiourea (Table 1).

1.7.3 Fourier Transform Raman analysis

Fig. 4 shows the FT-Raman spectrum of TTPI doped KCL crystal. Generally, the N-H stretching vibrations occur in the region 3400-3000 cm^{-1} (Lorenc, 2012). In our case, the observed band at 3250 cm^{-1} in FT-Raman spectrum is assigned to stretching frequency of N-H group.

IV. OPTICAL STUDIES

2.7.4.1 UV-Visible Analysis

Figure 5 elucidates that the UV-Vis–NIR absorption spectra were recorded in the wavelength range 200 to 800 nm, the optical properties of the crystals were examined using LAMBDA-35 UV-Vis spectrometer. The synthesis crystal reveals wide transmission window in the visible and NIR regions. The UV-visible enables them to be probable candidates for opto-electronic application (Dhunane *et al.*, 2008).

The optical absorption spectrum of tetrathiourea potassium lodide doped kcl. The cut off wavelength was found to be 277 nm. The crystal has very low absorption in the entire visible and NIR regions spectra. The large transmittance window in the visible and NIR region allow a good optical transmission for the second harmonic frequencies. This crystal is essentially used in optical applications and therefore, optical transmittance gap and the transparency lower cut off (200 to 400 nm) is very significant for the understanding of SHG amount produced in this range using diode lasers.

2.7.4.2 PL Study

The PL region emission should be attributed to the radioactive annihilation of excitons, and the peaks in the blue emission band might originate from the ionized oxygen vacancies to the valence band. The visible emission is caused by the radioactive recombination of a photo generated hole with an electron occupying the oxygen vacancy (Gnanam and Rajendran, 2011). Fig. 6 shows the emission bands ranging from 250 to 650 nm for TTPI doped KCL crystal can be due to transitions from different levels. The PL bands ranging from 354 to 551 nm for the sample could be the result of defects, including oxygen vacancies in the crystal.

2.7.4.3 Micro-Hardness Studies

The Vickers hardness testing of 0.2 mol% TTPI doped KCL crystal is done by Futuretech FM-800 type E-series microhardness analyzer. The mechanical strength of the doped KCL crystal was observed by applying loads of 20 g, 40 g and 60 g for constant indentation time 5 Second. The Vickers microhardness value was calculated using formula

$$H_v = 1:8544\ (P/d^2)$$

where, p is the applied load (g) and d is the standard diagonal length (mm) of the groove mark (Senthil *et al.*, 2014). The plot of Vicker's hardness (Hn) versus load (P) for doped KCL crystal is shown in Fig. 7. From the profile, it is observed that hardness decreases with load increases up to 70 gm, no cracks have been observed, which is moderately harder. The relation between the load (p) and indentation diagonal length as (d) is given by Meyer's law as

$$p = k_1 x\ d$$

where, n is Meyer index. According to Onitsch criterion, the calculated n value found to be 4.5, which suggests that the grown crystal belongs to soft material.

2.7.4 Nonlinear Optical Technique

The second harmonic generation (SHG) exchange competence of TTPI was measured by Kurtz and Perry powder technique. The NLO efficiency of the grown sample was measured by Kurtz powder (Kurtz and Perry,

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1968) method using Nd:YAG laser as the source. The crystal was stranded into a homogenous powder of particles and compactly packed between two transparent glass slides. Q-switched Nd:YAG laser emitting a necessary wavelength of 1064 nm (pulse width 8 ns) was allowed to strike on the sample cell normally. The SHG output 532 nm (green light) was finally detected by the photomultiplier tube. The discharge of green radiation from the TTPI crystal confirms the second harmonic generation in this crystal. It is a potential material for frequency conversion.

2.7.5 Thermo gravimetric analysis and Differential thermal analysis

The thermal behavior of the synthesis crystal was analysis by Perkin-Elmer thermal analyzer (STA 409 PC). The thermal behavior of TTPI doped Kcl crystal was analyzed by thermogravimetric analysis (TG) and degree of difference thermal analysis (DTA) at a heating rate of 50 ml/min in the range of 35˚C and 800˚C in the nitrogen atmosphere. Thermogravimetric (TG) and differential thermal analysis (DTA) analysis was carried out using Perkin-Elmer thermal analyzer (STA 409 PC) The analysis of TGA curve reveals that decomposition of doped crystal is started from temperature 225˚C. The major weight loss of the doped Kcl crystal is observed in the temperature range 225˚C to 305˚C hence there is no mass reduction or disintegration up to 225˚C. In DTA curve the melting point of doped crystal is observed at 235˚C. The endothermic peak at 225˚C shows that melting point of potassium tetrathiourea chloride doped Kcl crystal. The results of TG-DTA analysis shows grown crystal have very good thermal stability, which has scope in NLO applications (Fig. 4.8) (Mallinga and Joseph, 2015).

2.8. Dielectric studies

The dielectric constant and loss factor of undoped and sodium sulfate doped TTPI crystals were measured using the parallel plate capacitor method at various temperatures ranging from 40 to 400 ^oC using an Agilent 4284A LCR meter at different frequencies ranging from 102 to 106 Hz.

The dielectric measurements were performed on a tetra thiourea potassium iodide doped KCL crystal can be measured dimensions of 9×5×1 mm^3. The dielectric constant and dielectric loss has been estimated using the relation (1) and (2).

$$\varepsilon = Cd/A\varepsilon 0 \quad \text{--- (1)}$$

$$\varepsilon = \varepsilon \tan\delta \quad \text{--- (2)}$$

at this juncture, C, is a capacitance of pellet in farad (F), d is the thickness of the crystal, A is the area of the crystal, and $\mathcal{E}_o$, is the permittivity of free space (ε_o = 8.86 X10^{-12} F/m).

The dielectric constant and loss factor of tetra thiourea potassium iodide doped KCL crystals is recorded in the frequency range from 50Hz-5MHz were measured using the parallel plate capacitor method at various temperatures ranging from 40 °C, 100 °C, 200 °C, 300 °C and 400 °C.

The opposite faces of the sample crystal were coated with top finest silver paste to obtain a brilliant responsibility surface layer. The variations of dielectric constant and dielectric loss factor as a function of frequency at different temperatures are obtainable in the figure 9.

From the consequences, its miles located that tetra thiourea potassium iodide doped KCL crystals; the dielectric steady and loss factor are determined to be increasing. The increase in dielectric constant with temperature is normally attributed to the crystal enlargement, the electronic and ionic polarizations and the presence of impurities and crystal defects. The growth at higher temperatures is particularly attributed to the thermally generated charge providers and impurity dipoles. The variations of dielectric constant with frequency and temperature showed the type of contributions that are present system (Selvarajan *et al.*, 1994).

V. Conclusion

The synthesized crystals of TTPI doped Kcl were synthesis by slow solvent evaporation technique at room temperature using solvent as water. The powder X-ray analysis shows the good crystalline in nature. The symmetric and asymmetric C=N stretching vibration at 737 and 1460 cm^{-1} of thiourea molecules are shifted to 790 and 1360 cm^{-1} respectively. The UV-Vis-NIR spectra confirm that TTPI doped Kcl crystal are visible in the entire visible region and its lower cut-off values are 277 nm respectively. The analysis of TGA curve reveals that decomposition of doped crystal is started from temperature 225˚C. The major weight loss of the doped Kcl synthesis crystal is observed in the temperature range 225˚C to 305˚C hence there is no mass reduction or decomposition up to 225˚C. Onitsch criterion, the calculated n value found to be 4.5, which suggests that the grown crystal belongs to soft material.

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Table 1. FT-IR spectral assignments of TTPI doped KCL

Wavenumbers (cm^{-1})	Assignments
737	Symmetric C-N stretching
1460	Asymmetric C-N stretching
1360	Thiourea shift
3200	N-H absorption
3000	Metal thiourea

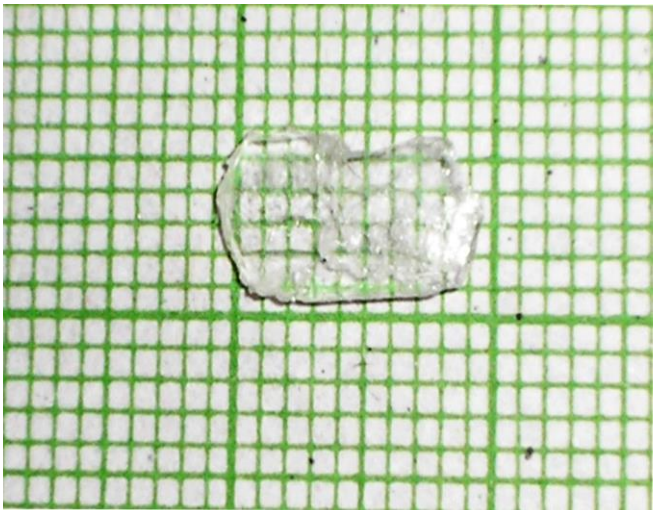

Figure 1. Grown crystal of TTPI

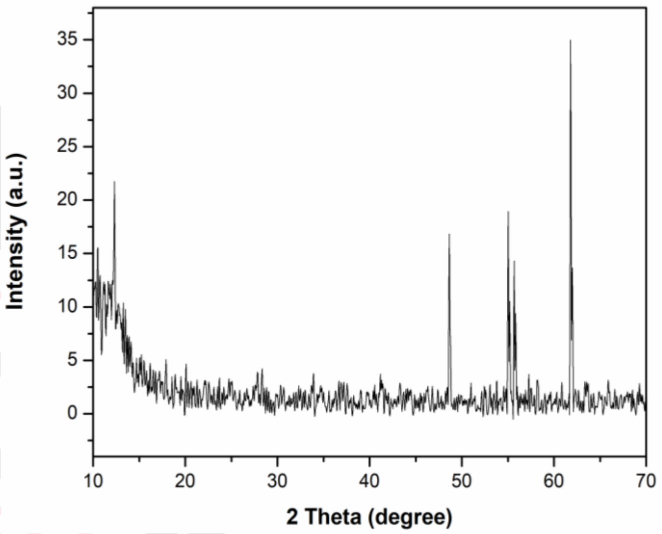

Figure 2. The XRD pattern of TTPI doped Kcl crystal

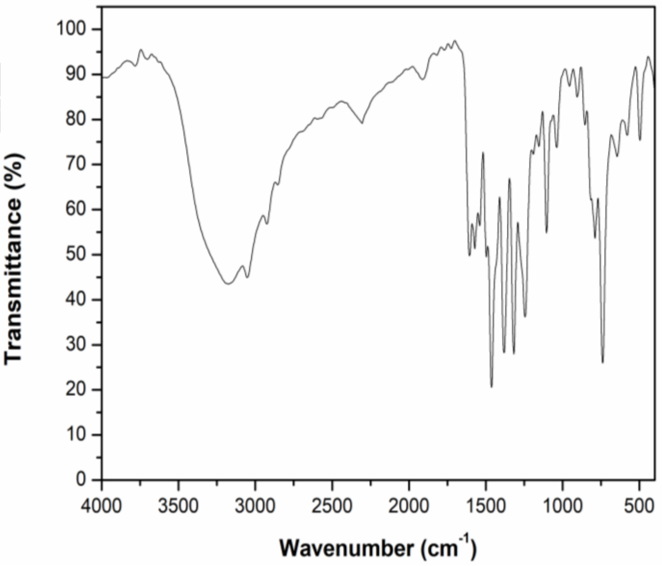

Figure 3. The FT-IR spectrum of TTPI doped KCL crystal

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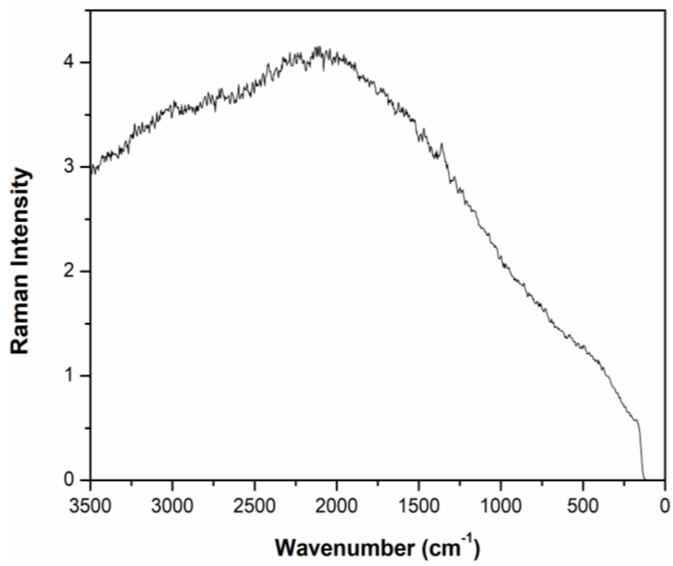

Figure 4. The FT-Raman spectrum of TTPI doped Kcl crystal

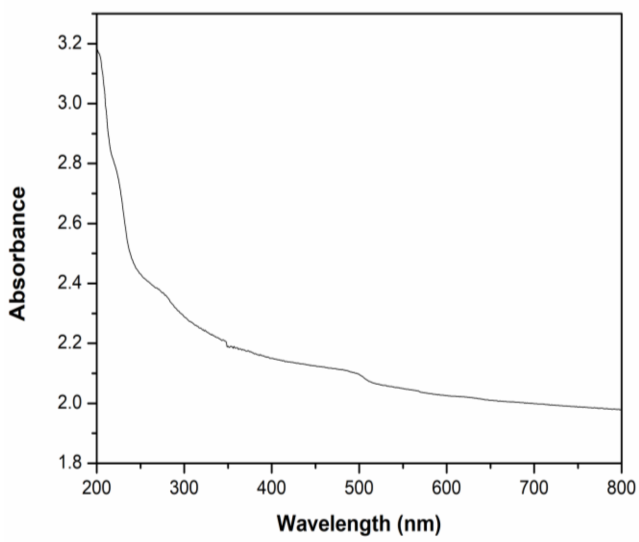

Figure 5. The UV-Visible spectrum of TTPI doped Kcl crystal

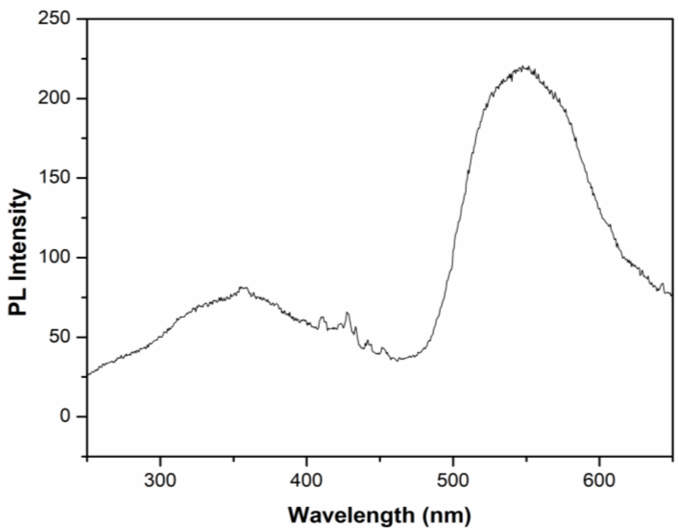

Figure 6. The PL spectrum of TTPI doped Kcl crystal

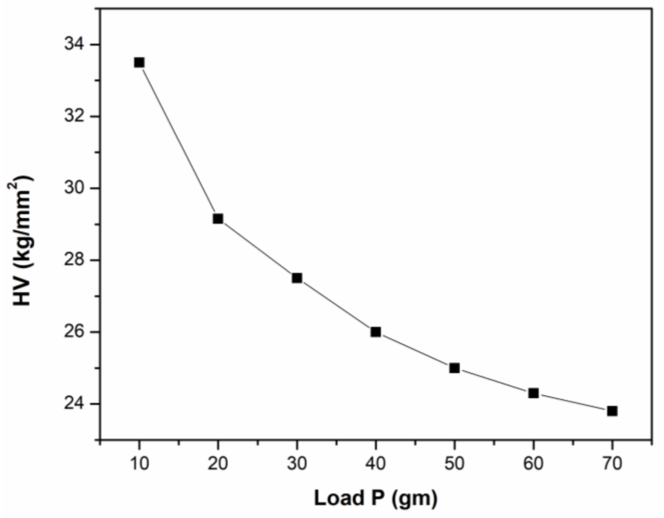

Figure 7. The Hardness test of TTPI doped Kcl crystal

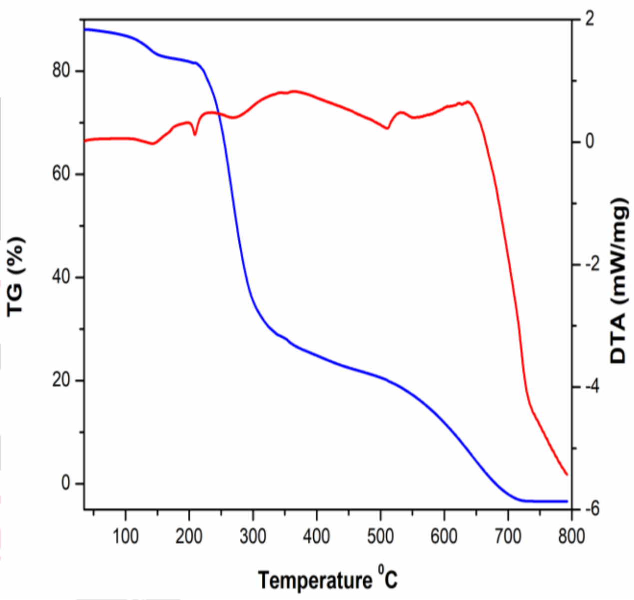

Figure 8. The TG-DTA analysis of TTPI doped Kcl crystal

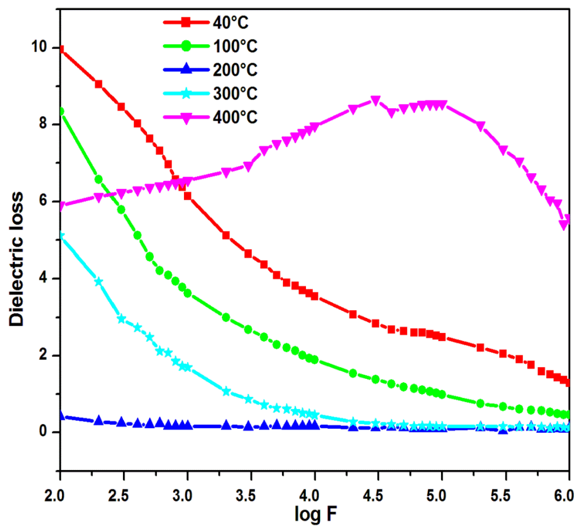

Figure 9. Dielectric Loss with Log F of Tetrathiourea Potassium Iodide Doped Kcl Crystals for Different Temperature

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