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Summary of Known Linear and Nonlinear Optical Properties of LiInS_2

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Advanced Applications
Laser and Environmental Programs

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TO: Stephan Velsko, L-495
FROM: Chris Ebbers
SUBJECT: Summary of known linear and nonlinear optical properties of LiInS_2

Summary

LiInS_2 is a potentially useful crystal for cascaded parametric frequency conversion in the mid-IR. It is nearly noncritically phasematched for 1.064 μm pumped, degenerate 2.12 μm generation and 2 micron pumped generation of 3-5 μm light. The nonlinear optical coefficients are 2x larger than those of KTP or KTA, while the transparency extends from 0.5-8 μm . LiInS_2 crystals are currently available in volumes up to 5 mm^3 . This memo provides a brief summary of the current literature concerning the growth and linear and nonlinear optical properties of LiInS_2 .

Growth

LiInS_2 is a congruently melting compound which crystallizes with point symmetry $\text{mm}2$ and is isostructural with LiGaO_2 , LiGaS_2 , LiInSe_2 , and LiInTe_2 . It is grown at temperatures around 880° C by directional solidification in graphite (or tantalum) crucibles.¹⁻⁹ The starting components for the growth runs are typically metallic Li, S, and In_2S_3 . The initial reaction of the starting components is highly exothermic, perhaps similar to the growth of ZnGeP_2 . Growth is complicated by the high vapor pressure of the melt as well as the reactivity of molten Li, which readily oxidizes, as well as attacks standard crucible materials such as Pt.

General Properties of LiInS_2

LiInS_2 is a rarity among materials potentially useful for mid infrared nonlinear optics in that it is optically biaxial. Optically biaxial materials are of interest due to the possibility of thermally insensitive phasematching directions, that is, propagation directions in which the phasematching thermal bandwidth is very large. LiInS_2 is transparent from approximately 500 nm to 9 μm ($\alpha <$

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10%/cm). Mention is explicitly made that the material does not appear to have the structural defects (high conductivity) associated with AgGaS₂ type compounds. The resistivity has been measured in 3 different references to be $>10^{11} \Omega\cdot\text{m}$. No photoconductivity in the crystal is observed. Unfortunately, the small electro-optic coefficients would make LiInS₂ a poor choice as an electro-optic material. The material has a "high" hardness. Crystals are transparent (or slightly yellow), and are stable in air, water, toluene, etc. Crystals may be etched in HNO₃ or bromine. The size of the crystals obtained in Ref. 10 is not mentioned, although a prism and 2 (thin) 5° wedges were fabricated. Other references¹⁻⁹ have obtained crystals 4x4x5 mm³. (Additional comment: I contacted G.D. Boyd.¹⁰ He recalls that the material was sufficient to cut a prism around 5 mm on a side).

Linear and Nonlinear Optical Properties

The linear and nonlinear optical properties of LiInS₂ have been measured in References 10-12. The refractive indices have been measured¹⁰ from 450 nm to 11 μm . Using these values for the refractive index, we have obtained the best fit parameters of Table I to the 4 parameter Sellmeier equation (1). The Z or 2-fold axis is coincident with n_γ , X is coincident with n_β , and Y is coincident with n_α , where $n_\alpha < n_\beta < n_\gamma$. By symmetry, nonlinear coupling in the principal planes vanishes for propagation down the Z axis and is significant only for Type II and Type III interactions. The birefringence of the γ - β birefringence is small, thus phasematching in this principal plane will have a large angular acceptance (small angular sensitivity).

$$n^2 = A + \frac{B}{C + \lambda^2} + D\lambda^2 \quad (1)$$

Table I. Sellmeier parameters (1) for LiInS ₂			
	α or Y	β or X	γ or Z or 2 fold axis
A	4.418222	4.559534	4.59206
B	0.1254461	0.1403701	0.1410887
C	-0.0657432	-0.069233	-0.069287
D	-0.0028850	-0.0028731	-0.0030589

The loci for a Type II, 1.064 μm pumped OPO are displayed in Figure 1 for generation of signal between 3.5 and 2.4 μm . The noncritical wavelength for propagation down the β dielectric axis is 2.29 μm for Type II doubling. Thus, LiInS₂ is nearly non-critically phasematched as a 1.064 μm pumped, Type II degenerate OPO down the β dielectric axis. As displayed in Figure 2, LiInS₂ is also non-critically phasematched for Type II generation of 3 and 5 micron light (signal

and idler) from a 2.12 micron pump. The thermal behavior of the indices of refraction in LiInS₂ is currently not known. Angular sensitivity of phasematching in the β - γ plane is $\sim 250/\text{cm-rad}$ in the midsection of γ - α plane, and $\sim 860/\text{cm-rad}$ in β - α plane within 20° of β axis.

The nonlinear optical coefficients of LiInS₂ were measured at 10.6 and 1.06 μm using the wedge technique,¹⁰ relative to d_{14} of GaAs. Uncertainty in the value of d_{14} of GaAs ranges from 90-134 pm/V.^{10,15} Using the value $d_{14} \sim 134$ pm/V gives for LiInS₂:

$$d_{\gamma\gamma\gamma} = 18 \text{ pm/V}$$

$$d_{\gamma\beta\beta} = 15 \text{ pm/V}$$

$$d_{\gamma\alpha\alpha} = 9.7 \text{ pm/V at } 10.6 \mu\text{m}$$

This may be compared to $d_{14} \sim 111$ pm/V for ZnGeP₂. However, for a noncritically pumped 1.06 micron to 2.12 micron application, LiInS₂ should be compared with LiNbO₃, KTP, and KTA. The effective nonlinearity in LiInS₂ is approximately 2x larger than that of KTA, KTP or LiNbO₃.

Availability

LiInS₂ is currently available in $\sim 5 \text{ mm}^3$ volumes from Japanese and former Soviet Union (FSU) sources. I have contacted Z. Z. Kish (Ref. 5, 7, 8, 9, and 12) formerly of Uzhgorod State University, now located in Canada. He indicated that only crypto-crystalline material is available from his institute, useful for semiconductor research. However, K. Kuriyama of Hosei University (Ref. 2-4) has indicated that he is interested in collaborating on research involving LiInS₂, and has pieces a few mm^3 in volume. We are also currently pursuing alternative sources in the Russia and United States.

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Attachments (2 Figures)

cc: Bill Krupke

NCPM Type II
2.295 μm
(X) BETA

LINS2

1.064 μm pump $\rightarrow$ X + { 3.5 - 2.5 μm }

Type II

If $\text{deg GaAs} = 90^\circ$

$drrr = 10.6 \text{ pm/V}$

$d\gamma_{\beta\beta} = 6.66 \text{ pm/V}$

$d\gamma_{\alpha\alpha} = 5.76 \text{ pm/V}$

Figure 1. Phasematching locus vs. signal generation for Type II, 1.064 micron pumped optical parametric interaction in LiInS2.

LINS2

X , BETA

2.12 μm pump $\rightarrow$ (idler, signal) μm

Figure 2. Phasematching locus vs. signal generation for Type II, 2.12 micron pumped optical parametric interaction in LiInS2.

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