

Poisson's Ratios of Technological Materials

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Abstract—Poisson's ratio (PR), the relation between lateral contraction of an elastic rod when subjected to a longitudinal extension, has a long and interesting history. For isotropic bodies, it can theoretically range from $+\frac{1}{2}$ to -1 ; the experimental gamut for anisotropic materials is even larger. For the vast majority of materials the PR is positive for all combinations of directions. But as far back as the 1800s, Voigt and others found that for some materials negative values were encountered. Negative PR (nPR) values remained for many years merely a curiosity, but more recently some of the interesting technological consequences have come to be recognized [1-3]. Some of the counterintuitive acoustic possibilities of nPRs are analogous, in a certain fashion, to those arising with negative refraction electromagnetic materials [4]. Even when a material does not have nPR properties, if it is piezoelectric, then the PR can be altered, sometimes by appreciable amounts, by changing the electrical boundary conditions [5-6]. We review Poisson's ratio in crystals, describing technologically important materials that have small, or negative PRs. Potential applications of the nPR property are also mentioned.

I. INTRODUCTION

Poisson's Ratio (ν) is defined as the ratio of lateral contraction to longitudinal extension strains when a bar is subjected to a terminal tractive load, in the limit as the cross-section vanishes [7]. Originally formulated for isotropic solids, the definition carries over logically to anisotropic bodies [8-9]. Isotropic bodies are constrained thermodynamically to the range $+\frac{1}{2} > \nu > -1$. Current interest centers around materials having PRs that exceed these limits by virtue of natural or artificial anisotropy [10-29]. Whereas laws of physics govern conservation of various fluxes (mass, energy, linear & angular momentum), there is no such law requiring the conservation of volume, and the variety of extant PR values stem from this fact. Of particular interest are nPR substances; these have been termed "auxetic" by Evans, et al. [18]. Some of the generic structures, attributes, and uses of such materials, particularly the auxetics, are the following.

Structures: Reentrant cellular foams, solids, and honeycombs, microporous polymers, laminates and

composites (specifically piezo-polymer), hinged structures, convoluted ribbed and chiral (helical) chains, Cosserat/Mindlin microstructural materials (45 constants), and ordinary crystals (Systems I to IX).

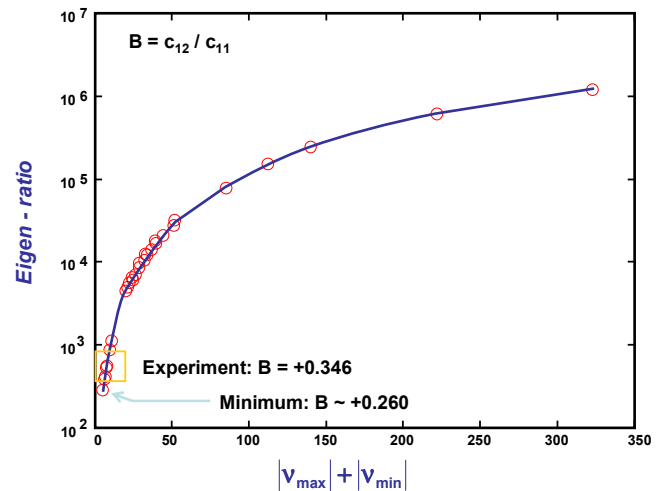


Figure 1. Eigen-ratio vs. PR for lanthanum niobate.

Conjectured attributes: Increased resilience, enhanced shear moduli, indentation resistance, fracture toughness, increased tear resistance, thermal shock resistance.

Conjectured uses: Micro- and nano-electronics; materials for substrate films; substrate/epitaxial layers subjected to temperature gradients, fluctuations; mitigation of force-frequency effect [30], which depends conjointly upon $c_{\lambda\mu\tau}$ and PR; study of structural phase transitions (austenitic-martensitic); increased stress decay rate with distance; ameliorated stress distributions around apertures and cracks (fracture mechanics); sandwich panels for aircraft and automobiles; piezocoupling enhancement in composites [3]; fasteners; miniaturized piezoelectric hydrophone sensors; enhanced dispersion, enabling acoustic sponges, shock-absorbers, air filters, etc.; novel acoustic transmission/reflection properties [31].

II. CRYSTALS [32-33]

We limit the discussion to crystals, described by a linear stiffness $[c]$ or compliance $[s]$ matrix. For crystals of arbitrary anisotropy, Bechmann tabulated the relations for rotations of these matrices, from which the PRs may be calculated [34]. PR requires specification of two orthogonal directions: the direction of tensile stress (that we take as the rotated X_1 axis), and the lateral direction of strain (taken as the rotated X_2 axis). The IEEE axial convention for three coordinate rotations is $(YXwlt)\phi/\theta/\psi$, specifying a first rotation about the X_3 axis by angle ϕ , a second rotation about the resulting X_1' axis by angle θ , and a third rotation about the resulting X_2'' axis by angle ψ [32-33]. In the resulting X''' coordinate system, the rotated X_1 axis is determined solely by the angles ϕ and ψ . Likewise, the rotated X_2 axis is determined solely by the angles ϕ and θ .

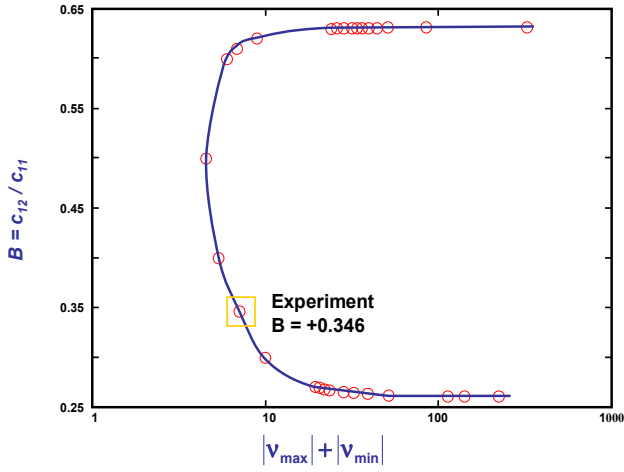


Figure 2. Change in PR by altering c_{12}/c_{11} .

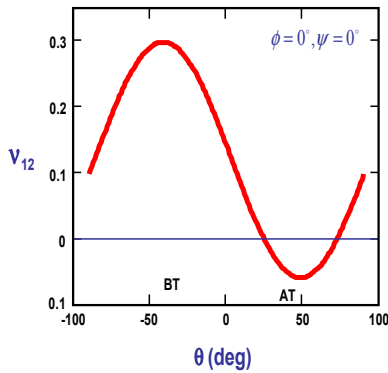


Figure 3. PR of alpha-quartz rotated-y-cuts.

θ	PR
24.5	0
35.3	-0.040
48.6	-0.059
72.6	0
49.2	0.291
0	0.141

Because the stored energy density of a crystal must be positive, the elastic matrix is constrained to be positive definite (PD) [35-36]. A matrix is PD iff: a) the principal minors are strictly positive, or b) the leading principal minors are strictly positive, or c) all eigenvalues (EVs) are positive. This last criterion was stated in equivalent terms for the elastic problem by Lord Kelvin [37]. We use this in the sequel; in particular, the ratio of the maximum to minimum EV is used to investigate the limits of stability and is correlated with magnitude of the PR. Whereas the EVs of $[c]$ and $[s]$ are different, this eigenvalue ratio (ER) is the same for both.

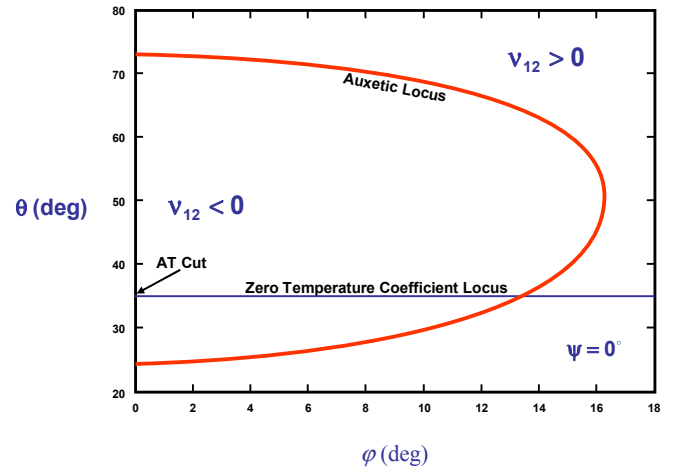


Figure 4. Auxetic locus of alpha-quartz for $\psi = 0^\circ$.

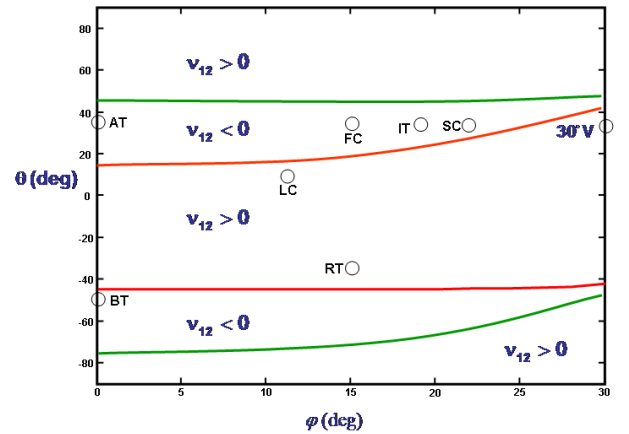


Figure 5. Auxetic Loci of alpha-quartz for $\psi = 90^\circ$

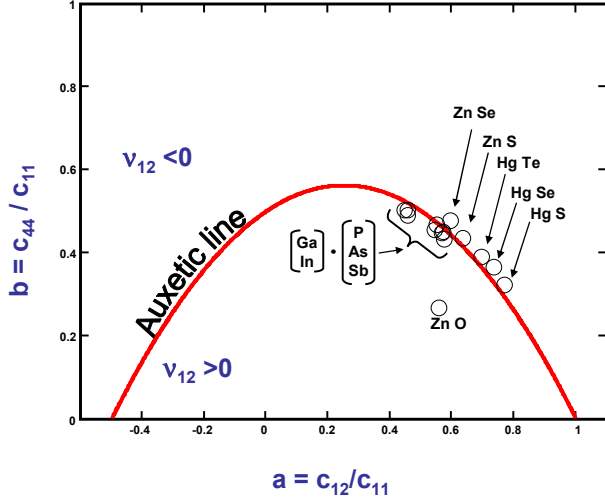


Figure 6. Binary semiconductors plotted with auxetic locus.

Tables 1, 2 and 3 list various PRs for a variety of crystals in the monoclinic, rhombic, and cubic systems. Data for these tables are taken from [38-39], which contain citations to the original literature. In each case the complete angle space was searched to find the maximum and minimum values of v ; also given are values for the aggregate $\langle v \rangle$, determined by the iterative procedure given in [40-41]. The listing of cubics has been chosen to contain only auxetics; $v_{[111]}$ is independent of rotation about the three-fold axis. The PR $v_{[100]}$ notation denotes that the two PR cubic axes are aligned along equivalent [100] directions.

The entries in Tables 1 and 2 are arranged in order of increasing ER; the symbol Σ denotes the sum of the absolute values of the PRs. One sees a rough correlation between these two measures. The last entry, LaNbO_4 , has a rather large value of PR. In Figure 1, its ER is plotted against Σ when the ratio $B = c_{12}/c_{11}$ is varied. The experimental value is shown to be close to the minimum ER. Figure 2 similarly plots B against Σ . It is seen that the PR increases to arbitrarily large values as the values of B reach the limits for lattice stability.

Table I. Poisson's ratios for some monoclinic crystals.

Material	Formula	Class	v_{\max}	v_{\min}	$\langle v \rangle$	Σ	eigen-ratio
diopside	$\text{CaMgSi}_2\text{O}_6$	2/m	+0.483	+0.100	+0.252	0.583	6.46
lithium sulfate monohydrate	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	2	+0.470	-0.027	+0.250	0.497	6.53
bismuth vanadate	BiVO_4	2/m	+0.682	-0.033	+0.248	0.715	6.6
cosite	SiO_2	2/m	+0.734	-0.109	+0.271	0.843	6.9
potassium tartrate hemihydrate	$\text{K}_2\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	2	+0.529	+0.139	+0.318	0.668	9.88
orthoclase	KAlSi_3O_8	2/m	+0.768	-0.169	+0.296	0.937	11.5
triglycine sulfate (TGS)	$(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$	2	+0.864	-0.040	+0.357	0.904	13.6
ethylene diamine tartrate (EDT)	$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_6$	2	+1.257	-0.005	+0.332	1.262	16.7
calcium sulfate dihydrate (gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	2/m	+0.704	-0.120	+0.341	0.824	17.2
zirconium oxide	ZrO_2	2/m	+0.581	-0.631	+0.267	1.212	21.7
d-tartaric acid	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6 = \text{C}_4\text{H}_4\text{O}_6$	2	+0.888	-0.211	+0.325	1.099	23.3
cesium deuterium selenite	$\text{Cs}_2(\text{SeO}_3)_2$	2/m	+1.030	-0.303	+0.377	1.333	28.5
sodium thiosulfate pentahydrate	$\text{Na}_2\text{S}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$	2/m	+1.264	-1.125	+0.363	2.389	34.8
cesium dihydrogen phosphate	CsH_2PO_4	2/m	+2.701	-1.926	+0.397	4.627	237
lanthanum niobate	LaNbO_4	2/m	+3.953	-3.011	+0.451	6.964	571

$\Sigma = |v_{\max}| + |v_{\min}|$

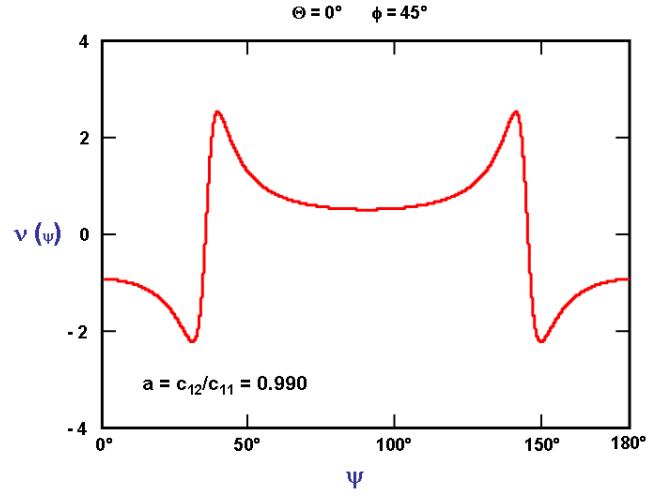


Figure 7. Poisson's Ratio for cubics with $\psi = 45^\circ$, $\theta = 0^\circ$ and c_{12}/c_{11} near the point of instability.

Table II. Poisson's ratios for some rhombic crystals.

Material	Formula	Class	v_{\max}	v_{\min}	$\langle v \rangle$	Σ	eigen-ratio
topaz	$\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$	mmm	+0.391	+0.069	+0.221	0.460	4.75
uranium	$\alpha\text{-U}$	mmm	+0.545	-0.017	+0.201	0.562	4.89
chrysoberyl	BeAl_2O_4	mmm	+0.293	+0.150	+0.229	0.443	5.00
barium sodium niobate (BSN)	$\text{Ba}_2\text{NaNb}_2\text{O}_{15}$	mm2	+0.385	+0.141	+0.239	0.526	5.69
forsterite	Mg_2SiO_4	mmm	+0.330	+0.138	+0.239	0.468	6.10
tellurium vanadate	$\text{Te}_2\text{V}_2\text{O}_9$	mm2	+0.442	+0.045	+0.199	0.487	6.64
aragonite	CaCO_3	mmm	+0.737	-0.062	+0.177	0.499	6.87
zinc antimonide	ZnSb	mmm	+0.460	+0.039	+0.255	0.499	7.64
lithium germanate	$\text{Li}_2\text{Ge}_2\text{O}_5$	mm2	+0.483	+0.150	+0.274	0.633	7.74
cadmium antimonide	CdSb	mmm	+0.612	+0.059	+0.237	0.671	9.35
polyvinylidene fluoride (PVDF)	$-(\text{CH}_2\text{CF}_2)_n-$	mm2	+0.690	-0.632	+0.343	1.322	10.7
lithium ammonium tartrate	$\text{LiNH}_4\text{C}_4\text{O}_6 \cdot \text{H}_2\text{O}$	222	+0.540	+0.107	+0.315	0.647	12.3
lithium formate	$\text{LiCOOH} \cdot \text{H}_2\text{O}$	mm2	+0.640	+0.096	+0.304	0.736	13.1
barite	BaSO_4	mmm	+0.616	+0.055	+0.318	0.671	13.8
β -resorcinol	$\text{C}_6\text{H}_4(\text{OH})_2$	mm2	+0.830	-0.084	+0.358	0.914	14.6
iodine	I	mmm	+1.311	-0.476	+0.277	1.787	15.3
sulfur	$\alpha\text{-S}$	mmm	+0.614	+0.101	+0.345	0.715	15.6
anhydrite	CaSO_4	mmm	+0.761	-0.047	+0.277	0.808	21.7
Rochelle salt	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	222	+0.866	-0.044	+0.386	0.910	35.1
sodium ammonium tartrate	$\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	222	+0.920	-0.084	+0.406	1.004	36.5

$\Sigma = |v_{\max}| + |v_{\min}|$

III. QUARTZ

The one trigonal entry that we have space to discuss is that old standby, α -quartz. In [42] are some admirable early and accurate PR calculations for quartz. Figure 3 shows the PR as function of the AT-BT angle θ , indicating the presence of auxetic behavior. The X_1 (digonal) axis is the direction of applied force, and the X_2' axis is the direction of the thickness of a resonator plate. In the auxetic region (including the AT cut), a compressional force will make the plate thickness diminish, and the frequency will increase. This lattice distortion is, in addition to the third-order elastic constants ($c_{\lambda\mu\tau}$), responsible for the force-frequency effect in resonators [30]. Figures 4 and 5 show the quartz auxetic loci when the angle of force application (ψ) is rotated in the plane of the plate. In Fig. 5 it is seen that the zero temperature locus (AT-FC-IT-SC cuts) is located within the auxetic region. The LC and RT cuts are nearly auxetic as well.

IV. CUBICS

For cubics, auxetic behavior may be examined by plotting $b = c_{44}/c_{11}$ versus $a = c_{12}/c_{11}$. Limits on a and b , dictated by energy considerations, are: $-1/2 < a < +1$ and $b > 0$. While the extrema of v_{12} are not necessarily those of v_{12} $\{[110][1\bar{1}0]\}$, this is ordinarily the case; in any event, the extrema lie on the periphery of the cubic primitive region circumscribed by the great circle paths from $[100]$ to $[110]$ to $[111]$ to $[100]$; see [27]. For this set of directions, the equation for v_{12} is $[(1-a)(1+2a) - 2b]/[(1-a)(1+2a) + 2b]$. The auxetic line ($v_{12} = 0$) has a maximum at $a = (1/2)^2$, $b = (3/4)^2$, and is plotted in Fig. 6 along with data points for an assortment of cubic semiconductors. Many III-V and II-VI binaries [43-44] lie close to the auxetic line. The unary semiconductors Si, Ge, and C(d) are not auxetic [45-46]. Global extrema are: Si ($v_{\max} = +0.360$, $v_{\min} = +0.065$); Ge ($v_{\max} = +0.363$, $v_{\min} = +0.025$); C(d) ($v_{\max} = +0.115$, $v_{\min} = +0.009$). For hexagonal (6/m mm), dislocation-free graphite, the corresponding figures are $v_{\max} = +0.860$, $v_{\min} = +0.004$; going from sp^3 to sp^2 makes quite a difference!

In Fig. 7 v is plotted for cubics vs angle ψ for $\phi = 45^\circ$ and $\theta = 0^\circ$. The value of $a = c_{12}/c_{11}$ is 0.990, a value bordering on the +1 limit for stability. One sees how the PR ratios increase beyond those for actual cubics given above; the extrema occur closer together as well. Whereas the PR bounds for isotropic substances is $-1 < v < +1/2$ for anisotropic elastic materials the bounds are [24] $-\infty < v < +\infty$; a somewhat larger gamut!

Table III. Poisson's ratios for some auxetic cubic crystals

Substance	v_{\max}	v_{\min}	$v_{[111]}$	$v_{[100]}$	$\langle v \rangle$
β -AgI	1.233	-0.415	+0.299	+0.466	+0.402
BN	0.236	-0.020	+0.071	+0.188	+0.121
BaTiO ₃	0.758	-0.162	+0.208	+0.395	+0.304
CdTe	0.698	-0.011	+0.295	+0.408	+0.351
CuCl	0.855	-0.070	+0.345	+0.444	+0.397
CuBr	0.911	-0.135	+0.328	+0.445	+0.391
CuI	0.704	-0.034	+0.281	+0.405	+0.343
β -HgS	0.799	-0.044	+0.329	+0.433	+0.383
HgSe	0.774	-0.055	+0.306	+0.423	+0.366
HgTe	0.713	-0.031	+0.289	+0.409	+0.348
LiF	0.422	-0.027	+0.144	+0.291	+0.211
MgAl ₂ O ₄	0.584	-0.070	+0.190	+0.353	+0.268
Ni	0.677	-0.085	+0.227	+0.384	+0.305
Ni ₃ Al	0.780	-0.178	0.208	0.398	0.307
β -SiC	0.397	-0.028	+0.133	+0.279	+0.198
β -cristobalite-1	0.176	-0.277	0.148	+0.121	-0.031
β -cristobalite-2	0.149	-0.296	0.173	+0.103	-0.054
β -ZnS	0.649	-0.025	+0.257	+0.388	+0.321
ZnSe	0.611	-0.035	+0.230	+0.371	+0.298

V. PIEZOELECTRIC CRYSTALS

In piezoelectrics, the electrical boundary conditions (BCs) must be taken into account [5-6]. The effect on PR of open-circuit (OC) and short-circuit (SC) BCs is shown in Table 4 for crystals with a variety of point group symmetries. The conditions OC and SC correspond, respectively, to imposition of constant D and E constraints.

VI. CONCLUSIONS

Bounds on Poisson's Ratio:

- Isotropics: $-1 < v < +1/2$ (known for many years)
- Crystals: $-\infty < v < +\infty$ (!) (known since 2005)

Artificially varying $c_{\mu\lambda}$ toward lattice instability produces large $|v|$ values:

- v_{\max} and v_{\min} increase in magnitude
- v_{\max} and v_{\min} draw closer in angle

Lattice stability is correlated with eigenvalue ratio:

- A crystal, like diamond, with EVs close to a six-dimensional sphere, is quite stable

Table IV. Effect of electrical boundary conditions on the PRs of various crystals.

Material	Class	T	$v_{\max}(E)$	$v_{\max}(D)$	$v_{\min}(E)$	$v_{\min}(D)$	$\langle v(E) \rangle$	$\langle v(D) \rangle$
			SC	OC	SC	OC	SC	OC
α -quartz	32	RT	+0.321	+0.316	-0.097	-0.102	+0.078	+0.076
β -quartz	622	600°C	+0.307	+0.307	+0.058	+0.058	+0.205	+0.205
α -TeO ₂	422	30°C	+1.455	+1.466	-0.767	-0.781	+0.333	+0.333
α -TeO ₂	422	0°K	+1.531	+1.542	-0.830	-0.844	+0.342	+0.341
LiNbO ₃	3m	RT	+0.388	+0.327	+0.137	+0.076	+0.251	+0.198
LiTaO ₃	3m	RT	+0.325	+0.365	+0.087	+0.032	+0.213	+0.189
ZnO bulk	6mm	RT	+0.417	+0.478	+0.295	+0.217	+0.353	+0.343
ZnO film	6mm	RT	+0.451	+0.503	+0.219	+0.160	+0.346	+0.335
LGS	32	RT	+0.581	+0.569	+0.093	+0.099	+0.337	+0.336
LGN	32	RT	+0.625	+0.611	+0.073	+0.079	+0.350	+0.348
LGT	32	RT	+0.590	+0.577	+0.101	+0.108	+0.348	+0.346
Pb ₂ KNb ₅ O ₁₅	mm2	RT	+0.476	+0.284	+0.124	+0.153	+0.258	+0.215
LiGaO ₂	mm2	RT	+0.258	+0.246	-0.030	+0.007	+0.148	+0.137
Li ₂ GeO ₃	mm2	RT	+0.338	+0.329	+0.090	+0.097	+0.243	+0.236

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