

Linear and nonlinear optical properties of quartz-type GaPO₄

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The linear and nonlinear optical properties of quartz-type GaPO₄ were studied. The indices of refraction (n_o and n_e) have been measured as a function of wavelength from 300 to 770 K. The second-harmonic-generation coefficient d_{11} and the Miller Δ_{11} have been determined experimentally in the temperature range from 300 to 1000 K. At higher temperatures, n_o , n_e , d_{11} , and Δ_{11} decrease slightly (Δ_{11} by approximately 6% at 1038 K). Compared with quartz or the isomorph berlinite, GaPO₄ shows very small variations with temperature. Theoretical calculations using Levine's bond-charge model have also been made for the temperatures 173, 293, 373, 773, and 1023 K. The results are in reasonable agreement with experiment and allow insight into the physical origin of the larger magnitude and considerably lower temperature dependence of d_{11} and Δ_{11} , as compared with quartz and berlinite.

I. INTRODUCTION

Among the metal orthophosphates $M^{3+}P^{5+}O_4$, with $M = \text{Al, Ga, Fe, or Mn}$, which crystallize in a quartz-type structure,¹ the gallium orthophosphate crystal α -GaPO₄ attracts increasing interest. There are two main reasons: the first is the recent discovery of the existence of crystal orientations with temperature-independent bulk wave resonance frequencies (e.g., the so-called AT cut),² and the second is the relatively large piezoelectric coefficient d_{111}^{piezo} , which shows a low temperature dependence over a very large temperature interval.³ In contrast to its isomorph AlPO₄, for which several reports exist concerning optical properties,⁴⁻¹⁰ little is known about the optical properties of GaPO₄.⁷

Our aim is to present experimental results on the linear (indices of refraction) and nonlinear optical properties of GaPO₄ [second-harmonic-generation (SHG) coefficient d_{111} and Miller⁵ Δ_{111}] and their temperature dependences, supplemented by theoretical calculations of d_{11} and Δ_{11} using Levine's¹¹ bond-charge model (here and in the following, we prefer the abbreviated notation with contracted indices).

According to the symmetry of α -GaPO₄ (D_{3h} or 32), there are two independent tensor elements: d_{11} and the Kleinman forbidden¹² d_{14} . In crystal class 32, the longitudinal third-rank tensor elements (e.g., piezoelectric e_{11} , electrooptic e_{11} , SHG d_{11}) are sensitive to the reversal of the diad axes. As a consequence, the measurement of d_{11} depending on temperature yields direct information on the order-parameter behavior related with the α - β phase transition, which has been fully exploited for quartz,¹³⁻¹⁵ and in a preliminary manner for AlPO₄.¹⁰ Since GaPO₄ does not undergo an α - β transition,¹ the corresponding information gained is pertinent to the α - β transition dynamics. It is a further purpose of the present work to discuss briefly the relationship between α - β transition dynamics and the temperature dependence of d_{11} .

II. EXPERIMENT

Three crystals of different thicknesses (0.566, 1.100, and 1.407 mm), grown by a hydrothermal synthesis method at AVL, have been used for the measurement of the room-temperature value of the SHG coefficient d_{11} of GaPO₄ by means of the Maker-Fringe (MF) method. One sample ($d = 1.407$ mm) has been used for the measurements of d_{11} covering a temperature range from 300 to about 1040 K. The samples were prepared as plane-parallel, Laue-oriented z -cut platelets. By use of ir techniques¹⁶ for a determination of the OH traces, typical values of about 100 ppm weight have been estimated for all specimens. All samples were investigated for the absence of twin domains¹⁷ by means of a polarization microscope after suitable etching. The principles of the MF technique used for the measurements are described in detail in Refs. 18-20. The main components of the experimental setup were (i) a repetitively pulsed Q -switched Nd-YAG laser (where YAG denotes yttrium aluminum garnet) of 1 MW power in the TEM₀₀₀ mode for the fundamental wave, (ii) a precision rotation table, and (iii) equipment for the detection and evaluation of the SHG signals.

The coherence length l_c was determined using two different procedures. The first step is to insert the experimental indices of refraction (measured by an autocollimation method using a coated half prism) into

$$l_c = \lambda / [4(n_\omega - n_{2\omega})], \quad (1)$$

where λ is the wavelength of the fundamental, and n_ω and $n_{2\omega}$ are the refraction indices of the fundamental and the second-harmonic waves, respectively. The second step is a determination of the coherence length from an analysis of the Maker-Fringe patterns by²¹

$$l_c \cong (\sin^2\theta_n - \sin^2\theta_{n+1})L / 4n_\omega n_{2\omega}. \quad (2)$$

L denotes the crystal thickness, and θ_n and θ_{n+1} are the

TABLE I. Summary of GaPO₄ bond properties.

<i>T</i> (K)	173	293	373	773	1023
$d^{\text{Ga-O}}$ (Å)	1.811	1.812	1.811	1.814	1.808
$d^{\text{P-O}}$ (Å)	1.527	1.529	1.522	1.530	1.525
$G_{111}^{\text{Ga-O}}$	0.101	0.0942	0.0933	0.0892	0.0808
$G_{111}^{\text{P-O}}$	0.111	0.1125	0.110	0.110	0.106
N_b (10^{28} m^{-3})	5.289	5.221	5.243	5.139	5.045
$E_h^{\text{Ga-O}}$ (eV)	9.111	9.099	9.112	9.074	9.149
$E_h^{\text{P-O}}$ (eV)	13.909	13.864	14.023	13.841	13.955
$C^{\text{Ga-O}}$ (eV)	12.297	12.327	12.349	12.354	12.556
$C^{\text{P-O}}$ (eV)	12.883	12.892	13.018	12.930	13.129
$f_i^{\text{Ga-O}}$	0.646	0.647	0.648	0.650	0.653
$f_i^{\text{P-O}}$	0.462	0.464	0.463	0.466	0.470
$\chi^{\text{Ga-O}}$	1.481	1.457	1.451	1.428	1.356
$\chi^{\text{P-O}}$	1.909	1.885	1.866	1.851	1.768
$\rho^{\text{Ga-O}}$	0.302	0.302	0.302	0.302	0.303
$\rho^{\text{P-O}}$	0.295	0.294	0.296	0.284	0.295
$q^{\text{Ga-O}}/e$	1.955	1.967	1.971	1.983	2.025
$q^{\text{P-O}}/e$	2.223	2.233	2.244	2.247	2.287

angles of two consecutive MF minima. Equation (2) is valid for small values of θ ; for higher values of θ the resulting l_c 's have to be corrected.

III. THEORY

The coefficient d_{11} and its temperature dependence can be calculated, e.g., by use of Levine's bond-charge theory.¹¹ The equations in SI units for d_{ijk} are

$$d_{ijk} = \sum_{\mu} F^{\mu} [d_{ijk}^{\mu}(C) + d_{ijk}^{\mu}(E_h)], \quad (3)$$

where F^{μ} is the fractional part of the bond of type μ , $d_{ijk}^{\mu}(C)$ is the ionic fraction of the nonlinear optical coefficient, $d_{ijk}^{\mu}(E_h)$ is the covalent fraction,

$$F^{\mu} d_{ijk}^{\mu}(C) = \frac{G_{ijk}^{\mu} N_b^{\mu} b^{\mu} e^{-k_s^{\mu} r_0^{\mu}} [Z_A^{\mu} + (n/m) Z_B^{\mu}] |e| (\chi_b^{\mu})^2 C^{\mu}}{2\pi (E^g)^2 (d^{\mu})^2 q^{\mu}}, \quad (4)$$

$$F^{\mu} d_{ijk}^{\mu}(E_h)$$

$$= \frac{G_{ijk}^{\mu} N_b^{\mu} s (2s-1) [r_0^{\mu} / (r_0^{\mu} - r_c^{\mu})]^2 f_c^{\mu} (\chi_b^{\mu})^2 \rho^{\mu} \epsilon_0}{d^{\mu} q^{\mu}}. \quad (5)$$

G_{ijk}^{μ} is the geometrical contribution of the bonds of type μ ,

$$G_{ijk}^{\mu} = 1/n_b^{\mu} \sum_m \alpha_i^{\mu,m} \alpha_j^{\mu,m} \alpha_k^{\mu,m},$$

where $\alpha_i^{\mu,m}$ denotes the direction cosine with respect to the i th coordinate axis of the m th of the n_b^{μ} bonds of type μ in the unit cell. N_b^{μ} is the number of bonds per m^3 , χ_b^{μ} is the macroscopic linear susceptibility of the bond (the total susceptibility is $\chi = \sum F^{\mu} \chi^{\mu} = \sum N_b^{\mu} \chi_b^{\mu}$), b^{μ} is the geometrical screening factor, $\exp(-k_s^{\mu} r_0^{\mu})$ is the Thomas-Fermi screening factor, and Z_A^{μ} and Z_B^{μ} are the number of core charges of atom A and atom B , respectively. $|e|$ is the electron charge, n/m is the stoichiometrical ratio of atoms A and B , C^{μ} is the ionic band gap of

TABLE II. Indices of refraction of α -GaPO₄.

λ (nm)	440		530		600		670		1060	
	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o	n_e
293	1.6207	1.6396	1.6135	1.6319	1.6074	1.6255	1.6031	1.6211	1.5935	1.6112
323			1.6131	1.6311			1.6029	1.6210	1.5924	1.6100
373	1.6190	1.6369	1.6099	1.6280	1.606	1.6236	1.6034	1.6211	1.5921	1.6101
423	1.6193	1.6377	1.6107	1.6290	1.6066	1.6204	1.6038	1.6218	1.5927	1.6103
473	1.6193	1.6379	1.6113	1.6295	1.6065	1.6253	1.6034	1.6214	1.5923	1.6102
523	1.6205	1.6388	1.6116	1.6290	1.6073	1.6250	1.6044	1.6219	1.5926	1.6103
573	1.6207	1.6389	1.6116	1.6293	1.6062	1.6242	1.6027	1.6200	1.5925	1.6102
628	1.6190	1.6382	1.6110	1.6286	1.606	1.6241	1.6037	1.6210	1.5920	1.6098
673	1.9193	1.6379	1.6107	1.6285	1.6063	1.6242	1.6033	1.6207	1.5917	1.6094
723	1.6196	1.6379	1.6107	1.6286	1.6063	1.6236	1.6031	1.6205	1.5918	1.6094
773	1.6197	1.6373	1.6114	1.6286	1.6044	1.6214	1.6029	1.6203	1.5917	1.6091

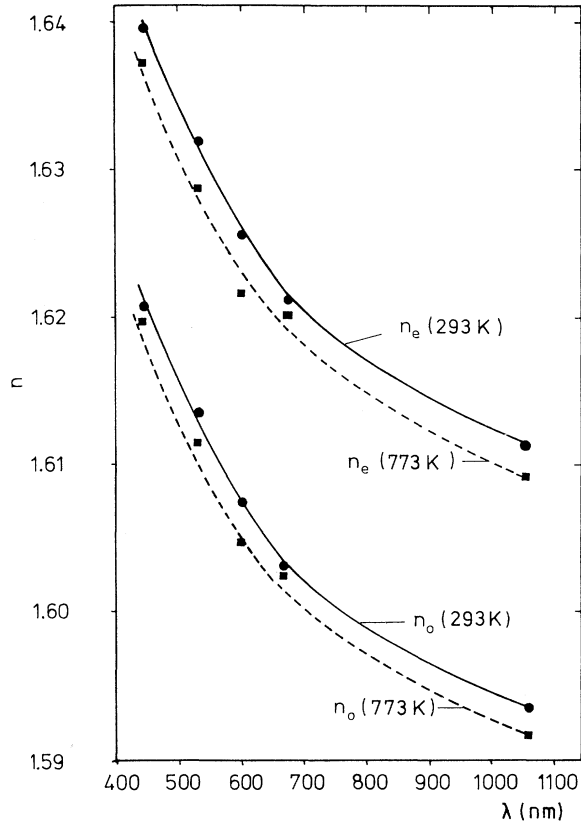


FIG. 1. Dispersion of the indices of refraction n_o and n_e at 293 and 773 K for α -GaPO₄.

the bond in eV, E_h^μ is the covalent band gap of the bond in eV, and E_g^μ is the resulting band gap of the bond in eV [$(E_g^\mu)^2 = (C^\mu)^2 + (E_h^\mu)^2$], $s = 2.48$ as given by Phillips.²² q^μ is the bond charge of the μ th bond, f_c^μ is covalency, $f_c^\mu = (E_h^\mu)^2 / (E_g^\mu)^2$, $\rho^\mu = (r_A^\mu - r_B^\mu) / d^\mu$, and r_A^μ and r_B^μ are the covalent radii of atom A and B. d^μ is the bond length in m, r_0^μ is the averaged radius of A and B in m, $r_0^\mu = 0.5d^\mu$, r_c^μ is the core radius, and $r_c^\mu = 0.35r_0^\mu$.

Structural data for $T = 197$ and 397 K are available from Ref. 23, and for $T = 293$, 773 , and 1023 K from Ref. 24. From these references, d^μ was taken and G_{11}^μ (Ref. 3) was calculated. Previously^{11,25} used for $b^{\text{Ga-O}}$ was $b^{\text{Ga-O}} = 0.58$, while for SiO₂, AlPO₄, and for the P—O bond in GaPO₄, $b^\mu = 0.66$.¹¹ Since there are good arguments for $b^\mu = \text{const}$ within a crystal class,¹¹ we suggest $b^{\text{Ga-O}} = 0.66$ also, which has the additional advantage of being much more consistent with the experimental χ . The b^μ are assumed to be independent of temperature, which can be justified by the fact that the coordination number (on which b^μ primarily depends) is also independent of T . The temperature dependence of ρ^μ (tetrahedral covalent radii²⁶ were used) is approximately given by $(\partial\rho/\partial T) = -(\rho/d^\mu)(\partial d^\mu/\partial T)$. All other quantities are calculated along the lines given in Refs. 11 or 25, for each of the temperatures mentioned above. The resulting input data for Eqs. (3)–(5) are summarized in

TABLE III. Measured coherence lengths of GaPO₄ at selected temperatures as determined from the Maker-Fringe minima. The error is about $\pm 0.4 \mu\text{m}$.

Sample	No. 1 (μm)	No. 2 (μm)	No. 3 (μm)
l_c (296 K)	15.1	15.1	15.1
l_c (573 K)	14.9	15.4	15.3
l_c (1038 K)		15.0	15.0

Table I. Using the same input data, the Miller Δ_{ijk} , which are related to the d_{ijk} by $d_{ijk} = \epsilon_0 \chi_{im}^{2\omega} \chi_{jn}^{\omega} \chi_{kp}^{\omega} \Delta_{mnp}$, are obtained from the ratio of the right-hand sides of Eqs. (4) and (5) to the product of the total macroscopic susceptibility χ cubed and ϵ_0 .

IV. RESULTS AND DISCUSSION

The indices of refraction for the ordinary (n_o) and the extraordinary ray (n_e) have been measured as a function of temperature in the wavelength region from 440 to 1060 nm in the range from room temperature to 773 K (Table II). For all wavelengths, n_o and n_e decrease slightly ($[n(293 \text{ K}) - n(773 \text{ K})] / \Delta T \approx 0.5 \times 10^{-5} \text{ K}^{-1}$). Figure 1 shows the dispersion of n_o and n_e at 293 and 773 K and the small decrease of the birefringence ($\Delta n / \Delta T \approx 0.25 \times 10^{-5} \text{ K}^{-1}$).

As is the case with the homeotype quartz and the isotype berlinite, GaPO₄ has no phase-matching directions for the fundamental wavelength $\lambda = 1060$ nm. The minimum difference between the index of refraction of the fundamental wavelength and of the second harmonic is found for the fundamental wave polarized perpendicular to the SH wave, and thus cannot be used for efficient generation of the SH.

The coherence length at 293 K according to Eq. (1) is $l_c^{(1)} = 14.1 \pm 1.5 \mu\text{m}$. Due to the small variations of n with T , a negligible temperature dependence of $l_c^{(1)}$ results. Both the 300 K value (15.1 ± 0.4 , Table III) and the temperature dependence of the coherence length $l_c^{(2)}$ are in accordance with the corresponding results for $l_c^{(1)}$. By extrapolating the indices of refraction to temperatures above 773 K, we calculated $l_c^{(2)}$ at all temperatures where a MF pattern was obtained. The coherence length turned out to be constant in the temperature range considered.

The ratio $d_{11} / d_{11}^{\text{quartz}}$ was determined in the temperature range from room temperature to 1040 K. The corresponding results can be found in Table IV and are displayed in Fig. 2, where the results are displayed normalized to the value at 300 K. The decrease of d_{11} over this very large interval is only about 7%. Since l_c is sufficiently low, the sample is thick enough, and, most important, the temperature range is ample (293–1073 K), we observe “temperature fringes” at a fixed angle of incidence (Fig. 3). Together with a constant value of l_c , this is an experimental proof of the slow decrease of d_{11} with temperature.

The upper temperature limit of the measurement is due

TABLE IV. Measured ratio $d_{11}(\text{GaPO}_4)/d_{11}(\text{quartz})$, "measured" (meas.) $d_{11}(\text{GaPO}_4)$ using the quartz reference value $d_{11}(\text{quartz})=0.335 \times 10^{-12}$ (Ref. 23), calculated $d_{11}(\text{GaPO}_4)$, and the corresponding values normalized to their room-temperature values.

T (K)	$d_{11}^{\text{GaPO}_4}/d_{11}^{\text{quartz}}$	d_{11} (10^{-12} m/V)		d_{11}/d_{11} (RT)	
		meas.	calc.	meas.	calc.
173			1.030		1.05
293	2.966	0.994	0.992	1	1
323	2.959	0.991		0.997	
373	2.944	0.986	0.961	0.992	0.98
398	2.938	0.984		0.990	
473	2.917	0.977		0.983	
523	2.903	0.973		0.978	
573	2.889	0.968		0.974	
623	2.875	0.963		0.969	
673	2.862	0.959		0.965	
773			0.928		0.93
833	2.819	0.944		0.950	
883	2.806	0.940		0.946	
933	2.792	0.935		0.941	
1023			0.80		0.80
1038	2.770	0.928		0.934	

to the onset of "water trace precipitation" effects originating from OH^- impurities, which are responsible for "milky" samples. The typical behavior was observed on an additional sample, where the temperature limit was found to be around 1120 K (for this temperature, Maker-Fringes with scattering-reduced SH intensity were recorded). However, the milky appearance of the crystal subjected to the water trace precipitation effect was less severe in the "high-quality portions" of the crystal, so

that complete opacity remained restricted to regions near growth zone boundaries and the seed. We note that the transformation of $\alpha\text{-GaPO}_4$ to the cristobalite form (see Ref. 1) has been observed in the microscope, evidenced by large white bubbles appearing on raising the temperature beyond 1350 K.

A small decrease of d_{11} with T also results from the theoretical calculation (Table IV). Since the theoretical values are on an absolute scale, the experimental results

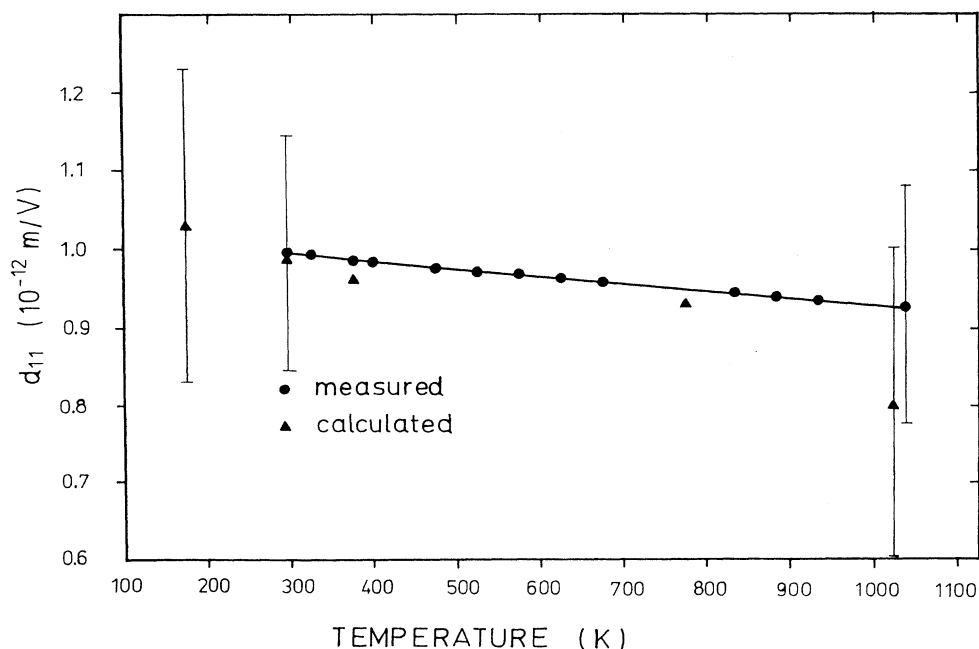


FIG. 2. Temperature dependence of the SHG coefficient d_{11} of $\alpha\text{-GaPO}_4$: ●, experimental; ▲, calculated.

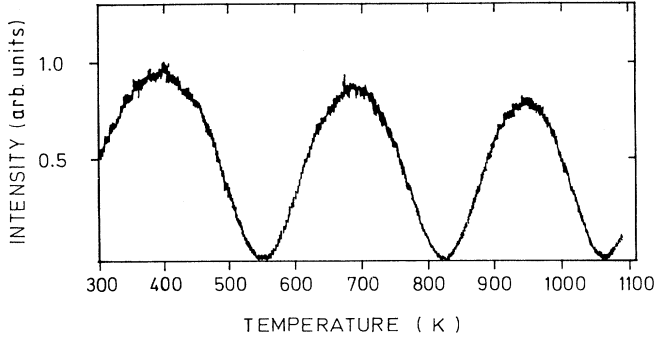


FIG. 3. Variation of the SHG intensity (in arbitrary units) with temperature for constant incidence angle of the fundamental wave (near plate normal) for α -GaPO₄.

have to be converted. Using the reference value $d_{11}^{\text{quartz}} = 0.335 \pm 0.016 \times 10^{-12}$ m/V,²⁷ $d_{11} = 0.99 \pm 0.18 \times 10^{-12}$ m/V is the experimental value at 293 K to be compared with the theoretical $d_{11} = 0.99 \pm 0.25 \times 10^{-12}$ m/V. For a comparison of the results with data of other crystals, the Miller Δ_{11} formulation⁷ is appropriate. The corresponding results, both experimental and theoretical, are shown in Table V.

The present result for GaPO₄ at room temperature is $\Delta_{11} = 2.97 \pm 0.6$ m²C⁻¹, and is somewhat larger than the corresponding values of the isotypic AlPO₄ ($\Delta_{11} = 2.25 \pm 0.5$ m²C⁻¹) (Ref. 10) and the homeotypic quartz ($\Delta_{11} = 1.50 \times 10^{-2} \pm 0.07$ m²C⁻¹).²⁷ According to Eqs. (3)–(5), the magnitude of the coefficient d_{11} is given by the longitudinal nonlinear susceptibility of the bond μ , by the geometrical weight G_{111} of the bond, and by the bond density N_b . All of these are larger in GaPO₄ than

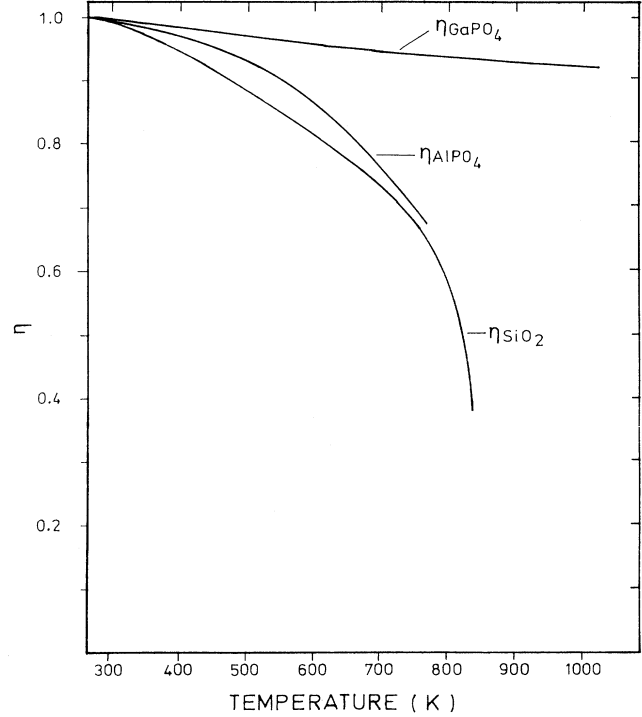


FIG. 4. Comparison of the normalized temperature dependence of the SHG coefficient $\eta = d_{11}/d_{11}(300 \text{ K})$ of α -GaPO₄ (this work), α -AlPO₄ (from Ref. 10), and α -quartz (from Ref. 13).

the corresponding values in quartz and in berlinite, in particular the covalent contributions to the bond nonlinearities $\beta^\mu(E_h)$ ($\beta^\mu = F^\mu d_{ijk}^\mu / N_b^\mu G_{ijk}^\mu$). The latter factor is responsible for the reduced cancellation of the homopolar and heteropolar contributions $F^\mu d_{111}(E_h^\mu)$ and

TABLE V. Measured ratio $\Delta_{11}(\text{GaPO}_4)/\Delta_{11}(\text{quartz})$, “measured” $\Delta_{11}(\text{GaPO}_4)$ using the quartz reference value $\Delta_{11}(\text{quartz}) = 1.50 \times 10^{-2}$ m²C⁻¹ (Ref. 23), calculated $\Delta_{11}(\text{GaPO}_4)$, and the corresponding values normalized to their room-temperature values. For $T > 775$ K, extrapolated values of $n_{2\omega}$ and n_ω have been used for the column “meas.”

T (K)	$\Delta_{11}^{\text{GaPO}_4}/d_{11}^{\text{quartz}}$		Δ_{11} (10 ⁻² m ² C ⁻¹)		Δ_{11}/Δ_{11} (RT)	
	meas.		meas.	calc.	meas.	calc.
173				2.390		0.993
293	1.982		2.973	2.406	1	1
323	1.977		2.966		0.998	
373	1.969		2.954	2.383	0.994	0.990
398	1.966		2.949		0.992	
473	1.955		2.932		0.986	
523	1.947		2.921		0.983	
573	1.939		2.908		0.978	
623	1.932		2.898		0.975	
673	1.926		2.889		0.972	
773				2.382		0.990
833	1.899		2.848		0.956	
883	1.889		2.834		0.953	
933	1.881		2.821		0.949	
1023				2.371		0.985
1038	1.863		2.794		0.940	

$F^{\mu}d_{111}(C^{\mu})$ as compared with quartz and berlinite, which yields a larger total bond nonlinearity for GaPO₄.

As can be seen from Table I, the temperature changes of the various factors used as input data for the bond nonlinearity are quite small. As a result, the decrease of the bond nonlinearity β^{μ} with T for both bonds is about 12% over the whole temperature range from 193 to 1023 K ($\beta^{\text{Ga-O}}$ decreases from 0.44 to 0.38 10^{-40} m⁴/V, $\beta^{\text{P-O}}$ from 0.68 to 0.61 10^{-40} m⁴/V). N_b also decreases because of the thermal expansion, which further lowers d_{11} . The third effect on the temperature dependence of d_{11} is due to the decrease of the structural factors G_{111}^{μ} (Table I), which in turn is related to the structural changes associated with the rotational motion ("back tilting") of the GaO₄ and PO₄ tetrahedra towards the prototypic β -phase symmetry. As in quartz¹⁵ and AlPO₄,¹⁰ these tetrahedra (point symmetry 2) are cooperatively rotated around the twofold axis, perpendicular to the threefold axis, thus defining a mean tetrahedral tilt angle δ . Indeed, the major structural change, which was observed in GaPO₄ up to 1023 K, is in essence the decrease of these mean tetrahedral angles δ of the GaO₄ and PO₄ tetrahedra (displayed in Ref. 24), which corresponds to incipient α - β

transition dynamics ($\delta_{\text{GaO}_4} \cong 21^\circ$ and $\delta_{\text{PO}_4} \cong 26^\circ$ at 293 K, $\delta_{\text{GaO}_4} \cong 18^\circ$ and $\delta_{\text{PO}_4} \cong 24^\circ$ at 1023 K,^{3,24} δ being zero in the hypothetical β phase). Since, again quite similar to quartz,¹⁵ G_{111}^{μ} is an odd function of the tetrahedral angles and is nearly insensitive to other structural changes (e.g., the tetrahedral distortions), any changes in δ affect G_{111}^{μ} and therefore influence d_{ijk} . The very small changes of δ in GaPO₄ as compared to quartz [δ_{SiO_4} decreases from 16° at RT to zero at 846 K (Ref. 15)] and to AlPO₄ [δ_{AlO_4} and δ_{PO_4} are zero above 858 K (Ref. 28)] are therefore the microscopic origin of the considerably smaller (Fig. 4) temperature dependence of d_{11} in GaPO₄.

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