JOURNAL OF MATERIALS SCIENCE 25 (1990) 4772–4775

Physical properties of hydrothermally grown gallium orthophosphate single crystals

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$GaPO_4$ single crystals have been hydrothermally grown by the horizontal temperature gradient method. The physical properties of these single crystals were measured. The following results were obtained: lattice parameters $a = 0.490\,nm$ and $c = 1.105\,nm$, density $\rho = 3.56\,g\,cm^{-3}$, Vickers hardness $H_v = 7.06 \times 10^9\,N\,m^{-2}$, refractive indices $n_e = 1.611 \pm 0.006$ and $n_0 = 1.599 \pm 0.006$, and birefringence $\Delta n = +0.012$. $GaPO_4$ single crystals exhibited some similar properties to α-quartz and $AlPO_4$ single crystals because of the similarity of their crystal structures.

1. Introduction

The low-temperature quartz type of $AlPO_4$ and $GaPO_4$ are known to have trigonal structure, and space group $P3_{2,1}21$. These single crystals are of interest because of the similarity of their crystal structures and properties to α-quartz. It is well known that the single crystals of $AlPO_4$ are attractive because of their superior electric character to α-quartz. $GaPO_4$ single crystals with a similar structure to $AlPO_4$ single crystals were expected to exhibit similar properties. In the present work, $GaPO_4$ single crystals were hydrothermally synthesized by the horizontal temperature gradient method in the low-temperature region [1–3]. The physical properties of single crystals of $AlPO_4$ and α-quartz have been extensively studied [4–8]. A number of measurements on $GaPO_4$ single crystals have also been obtained of lattice parameters, bond lengths, bond angles and the thermal expansion coefficients [1, 8, 9], but the physical properties of these single crystals have not been elucidated. This paper describes the results of measurements of lattice parameters, density, Vickers hardness, refractive index and birefringence of as-grown $GaPO_4$ single crystals, and compares them with those reported for α-quartz and $AlPO_4$ single crystals.

2. Experimental procedure

$GaPO_4$ single crystals were grown by the horizontal temperature gradient method. Hydrothermal crystal growth experiments were carried out at 180° C in 4M H_3PO_4. The crystals were grown in an autoclave using a silica glass capsule 15 cm long and 1 cm inner diameter. $GaPO_4$ particles, as nutrient, were placed in the low-temperature zone (i.e. dissolution region), while seed crystals were placed in the high-temperature zone (i.e. growth region), because of the negative solubility dependency of $GaPO_4$ on temperature in 4M H_3PO_4 solution [2]. With this arrangement it was expected that the dissolved nutrient would be efficiently used to grow single crystals on the seed without spontaneous nucleation occurring.

The analyses of as-grown single crystals were performed by X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier transform infrared spectra (FT-IR). The morphologies of as-grown single crystals were observed by optical microscopy.

The lattice parameters were determined by XRD at room temperature using a silicon standard. Density was measured using a pycnometer with distilled water at room temperature. In order to measure the Vickers hardness (H_v), as-grown single crystals were ground and polished. The values of H_v for a single crystal plate with polished surfaces along the c-axis were determined using a Hardness Tester MVK-G2 (Akashi). Measurements were made under the following conditions: indentation load 500 g, loading rate $0.06\,mm\,sec^{-1}$. The characteristic FT-IR spectra of as-grown single crystals were measured between 4000 and $400\,cm^{-1}$. The values of refractive index of the immersion liquids were confirmed using a refractometer. The two refractive indices of extraordinary (n_e) and ordinary light (n_0) were determined with a Becke line by the immersion method using a polarizing microscope. The birefringence was calculated from the refractive index values.

3. Results and discussion

Single crystals of $GaPO_4$ were successfully grown under the following conditions: temperature 180° C; horizontal temperature difference 40° C; run duration 7 days; solvent, 4M H_3PO_4 solution. Under these conditions, single crystals with euhedral morphology could be grown to about $5 \times 6 \times 4\,mm^3$ in size. The as-grown single crystals were confirmed by XRD to be only the low-temperature quartz type of $GaPO_4$ (Fig. 1).

Measurements of lattice parameters were carried out with Si(1 1 1) as an internal standard and the following values were determined: $a = 0.490\,nm$ and $c = 1.105\,nm$. These values agree very well with those reported by Goiffon *et al.* [8] and Litvin *et al.*[9]. The lattice parameters are also in good agreement with

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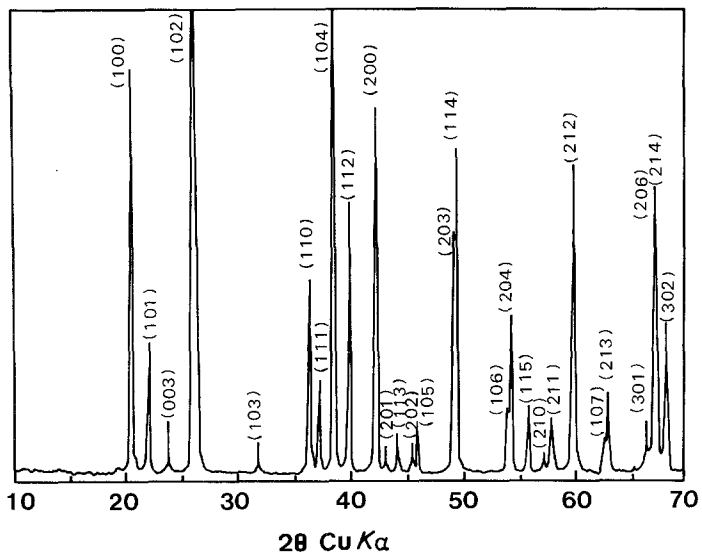

Figure 1 X-ray diffraction profile of $GaPO_4$ single crystals.

those for $AlPO_4$ (a = 0.494 nm, c = 1.094 nm) and α-quartz (a = 0.491 nm, c = 1.081 nm) [4–8]. Therefore, $GaPO_4$ single crystals may be expected to have close physical properties to α-quartz and $AlPO_4$ with the same space group. From the present lattice parameters results, the theoretical density was calculated to be 3.57 g cm^{-3}, which is in good agreement with the measured density of 3.56 g cm^{-3} at room temperature.

The values of hardness, H_v, for polished specimens were about 7.06 × 10^9 N m^{-2} at room temperature. The magnitude of hardness of the crystals depends strongly on factors such as the bond strengths between atoms in the crystallographic plane. These are considered to influence the bond type, bond length, charges, etc. Crystals of α-quartz, $AlPO_4$ and $GaPO_4$ are composed of partially covalent and ionic bonds. Of these crystals, α-quartz is a highly covalent compound in its bonding compared with $AlPO_4$ and $GaPO_4$ single crystals. In covalently bonded crystals, the higher bond strength typically leads to a higher hardness. From the present data it appears that the higher hardness of α-quartz (1.09 × 10^{10} N m^{-2}) reflects a higher bond strength than that of the $GaPO_4$ single crystals (7.06 × 10^9 N m^{-2}).

It is well known that the structure of M(1 1 1)PO_4, with M = aluminium, gallium, iron or manganese, consists of [MO_4] and [PO_4] tetrahedra arranged alternately and linked to one another at the vertices. In $AlPO_4$ and $GaPO_4$ crystals the P–O bond is more covalent than the Al–O and Ga–O bonds. The mean value of P–O bond lengths (0.152 nm) is shorter than the mean values of Al–O and Ga–O bond lengths, i.e. 0.173 and 0.181 nm, respectively [4, 8, 9]. Also, the mean value of O–Si–O bond angles (109.4°) is less than the mean values of O–Al–O and O–Ga–O, i.e. 110.1° and 110.3°, respectively [4, 5, 8, 9]. On the other hand, the ionicities of $AlPO_4$ and $GaPO_4$ single crystals are higher than that of α-quartz. The most important characters such as electromechanical coupling, are considered to be influenced by the degree of ionicity of the crystals. These facts indicate that the performance of device applications of $AlPO_4$ and $GaPO_4$ single crystals, as well as α-quartz, may probably be very promising.

Fig. 2 shows the FT–IR spectra of $AlPO_4$ (wet) [10] and as-grown single crystals of $GaPO_4$. The spectra are characterized by a strong absorption between 1250 and 1100 cm^{-1} due to P–O stretching and near 500 cm^{-1} due to O–P–O bending, and those in the region 700 to 600 cm^{-1} involve some combination of P–O and M–O (M = aluminium or gallium) stretching [10–16]. The hydroxyl groups contained in the $AlPO_4$ (wet) show a broad band at around 3400 cm^{-1} due to OH stretching. However, this band is not found in the as-grown single crystals of $GaPO_4$.

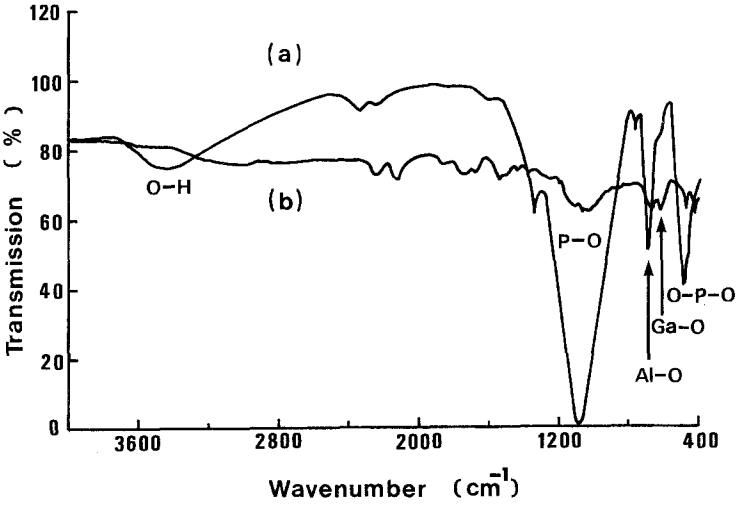

Figure 2 FT–IR spectra of (a) $AlPO_4$ (wet) and (b) as-grown single crystals of $GaPO_4$.

TABLE I Variation of the refractive index of $GaPO_4$ single crystals at room temperature

	Refractive index of immersion liquid					
	1.575	1.583	1.593	1.605	1.617	1.622
n_e	−	−	−	−	+	+
n_0	−	−	−	+	+	+

α-Quartz, $AlPO_4$ and $GaPO_4$ single crystals are known to be uniaxial birefringent crystals. The magnitude of the difference between the two refractive indices is referred to as the birefringence (Δn). This is defined by the equation $\Delta n = n_e - n_0$, where n_e is the refractive index of a light wave vibrating in a plane parallel to the optical axis and travelling in a direction perpendicular to it (i.e. extraordinary light), and n_0 is the index of a wave vibrating parallel to either of the other axes and travelling in the direction of the optical axis (i.e. ordinary light). Because these single crystals belong to the positive crystals, the value of n_e is higher than n_0, and the birefringence may show positive values. The immersion method was used to investigate the birefringence, with small single crystals of $GaPO_4$. The refractive indices of these single crystals were determined by carefully observing a Becke line. Table I shows the variation of the refractive index of $GaPO_4$ single crystals at room temperature. The values of n_e and n_0 are 1.611 ± 0.006 and 1.599 ± 0.006, respectively. These values are slightly higher compared to those reported [4] in α-quartz ($n_e = 1.544$, $n_0 = 1.535$) and $AlPO_4$ ($n_e = 1.529 \pm 0.003$, $n_0 = 1.519 \pm 0.003$). From these results, it is considered that the magnitude of the dielectric constant of $GaPO_4$ single crystals is relatively large than those of α-quartz and $AlPO_4$ single crystals. At room temperature and a frequency of 1 MHz, the values of dielectric constant for an electric field parallel and perpendicular to the c-axis are: α-quartz 4.6 and 4.4 [17], $AlPO_4$ 5.4 and 4.9 [18], $GaPO_4$ 10.3 and 7.8 [3]. The dielectric constant is also closely related to the refractive index in that direction.

Based on the values of the refractive indices, the value of birefringence is calculated to be +0.012. The magnitude of birefringence in the single crystal is usually determined by the polarization of ions in that compound. Because the polarizabilities of Si^{4+}, Al^{3+}, Ga^{3+} and P^{5+} ions are very small, it is considered that the values of birefringence are dependent mainly on O^{2-} ions. Therefore, it is reasonable to expect that the present value of +0.012 on $GaPO_4$ is close to those for α-quartz (+0.009) and $AlPO_4$ (+0.01) [4].

The linear thermal expansion coefficients ($\bar{\alpha}$) are also closely related to crystal structure, bond strengths and density. The density of $GaPO_4$ single crystals is relatively larger than that of α-quartz (2.65 g cm^{-3}) [4]. The values of linear thermal expansion coefficients for a- and c-axes on $GaPO_4$ were reported [1] as shown in Table II. These values for the a- and c-axes are 11% and 12%, respectively, larger than for α-quartz [4]. Also, these single crystals indicate an anisotropic property because of the dependence of anisotropic bond strength on direction.

The physical properties measured on $GaPO_4$ single crystals in this work are summarized in Table II. Although the crystal structure is similar, some of the resulting properties are slightly different from those of α-quartz and $AlPO_4$ single crystals. The difference is considered to be attributable to its different chemical features, such as chemical bonding, etc. $FePO_4$ and $MnPO_4$ single crystals, which have a similar structure to these single crystals, are also expected to exhibit similar properties to α-quartz, $AlPO_4$ and $GaPO_4$ single crystals.

TABLE II The physical properties of $GaPO_4$ single crystals

Lattice parameter (nm):	
a	0.490
c	1.105
V (nm^3)	0.2297
z	3
Density (g cm^{-3})	3.56
Hardness (N m^{-2})	7.06×10^9
Refractive index:	
n_e	1.611 ± 0.006
n_0	1.599 ± 0.006
Birefringence	+0.012
Thermal expansion coefficient (10^{-5} °C^{-1})	
α_a	1.79
α_c	0.46

4. Conclusion

$GaPO_4$ single crystals with euhedral morphology could be grown at 180° C in 4M H_3PO_4 solution. The physical properties of the as-grown single crystals were determined by the various measurements. Results obtained are as follows: lattice parameters, $a = 0.490$ nm, $c = 1.105$ nm; density, 3.56 g cm^{-3}; Vickers hardness, 7.06×10^9 N m^{-2}; refractive index, $n_e = 1.611 \pm 0.006$, $n_0 = 1.599 \pm 0.006$; birefringence, +0.012. The lattice parameters of $GaPO_4$ are similar to α-quartz and $AlPO_4$, but the density is relatively larger. The hardness of α-quartz is quantitatively higher than those of $AlPO_4$ and $GaPO_4$ single crystals. $GaPO_4$ single crystals have a similar birefringence to α-quartz and $AlPO_4$ single crystals. The linear thermal expansion coefficients for the a- and c-axes on $GaPO_4$ are 11% and 12%, respectively, larger than for α-quartz. These results indicate that $GaPO_4$ single crystals have similar properties to α-quartz and $AlPO_4$ single crystals because of their similarity in crystal structure.

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Received 5 June
and accepted 23 October 1989