Journal of Crystal Growth 501 (2018) 38–42

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Piezoelectric $Ca_3TaAl_3Si_2O_{14}$ (CTAS): High quality 2-in. single-crystal growth and electro-elastic properties from room to high (650 °C) temperature

Xiuwei Fu[a,*], Encarnación G. Víllora[a], Yoshitaka Matsushita[a], Yuuki Kitanaka[b], Yuji Noguchi[b], Masaru Miyayama[b], Kiyoshi Shimamura[a,c], Naoki Ohashi[a,d]

[a] National Institute for Materials Science, Tsukuba 305-0044, Japan
[b] Department of Applied Chemistry, The University of Tokyo, Bunkyo, Tokyo 113-8656, Japan
[c] Graduate School of Advanced Science and Engineering, Waseda University, Shinjuku, Tokyo 169-8555, Japan
[d] Materials Research Center for Element Strategy, Tokyo Institute of Technology, Midori, Yokohama 226-8503, Japan

ARTICLE INFO

Communicated by R.S. Feigelson

Keywords:
A2. Czochralski method
B1. Oxides
B2. Piezoelectric materials
B3. High temperature sensors

ABSTRACT

$Ca_3TaAl_3Si_2O_{14}$ (CTAS) single crystal is attracting much attention for high temperature sensor applications due to its high electrical resistivity and excellent piezoelectric properties. However, it is a big challenge to grow high quality CTAS single crystals. In this work, its growth conditions are optimized. Crack- and inclusion-free crystals are grown, achieving even a high quality single crystal with a width over 2 in. In addition, the temperature dependence of electro-elastic properties is systematically studied. This crystal presents a high thermal stability of structure and electro-elastic properties. The dielectric loss is less than 3% from room temperature to 650 °C. Therefore, CTAS single crystal is promising for high temperature sensor applications.

1. Introduction

In recent years, much efforts are being made to develop high temperature (HT) piezoelectric sensors for applications in aerospace, automotive industries, nuclear energy exploration, etc. [1–8]. HT piezoelectric combustion pressure sensors are relevant examples, because these are highly desired for combustion engines in order to increase the efficiency and to reduce the exhaust of harmful gases like CO_2 and NO_x [9]. In the operational temperature range, the piezoelectrics are expected to be free of phase transitions and pyroelectricity. In this sense, the conventionally common lead zirconate titanate (PZT) ceramics are discarded by their low Curie temperatures (ferroelectric to paraelectric transition points). The well-known α-quartz presents difficulties for HT applications due to its mechanical (ferrobielastic) twinning and its structural phase transition at around 300 and 573 °C, respectively [10]. On the other hand, the rare-earth calcium oxyborate crystals (RECOB) and ZnO are pyroelectric, which causes electrical noise for HT applications. In addition, though gehlenite $Ca_2Al_2SiO_7$ crystal doesn't have mentioned disadvantages, its distinct cleavage nature along the *c*-plane represents a serious drawback for practical applications [11]. Therefore, the demand for HT sensors encourages the development of efficient piezoelectrics that can stand device fabrication and operation temperature over 250 °C.

The langasite single crystals are widely investigated for HT sensor applications [1,12]. These compounds are non-pyroelectric and do not show any phase transitions up to their melting point (1300–1500 °C). Furthermore, the growth of large-size single crystals is feasible using the Czochralski (Cz) method. This family crystallizes in the trigonal space group *P*321 with the chemical formula $A_3BC_3D_2O_{14}$. There are four cationic sites: a decahedral site A, an octahedral site B, and two differentiated tetrahedral sites C and D [13]. Depending on the cation distribution, the langasite family is classified into two types: disordered and ordered. In disordered langasites there is a mixed site occupation, which generally leads to higher dielectric loss and lower electrical resistivity at HT. For example, $La_3Ta_{0.5}Ga_{5.1-x}Al_xO_{14}$ (LTGA, x = 0–0.5) is a well-known one, where Ga^{3+} occupies B, C and D sites randomly [14,15]. On the contrary, in ordered langasites each cationic site is occupied by a different element, each one fitting to the corresponding site so that a better performance can be obtained. Among this subfamily, $Ca_3Ta(Ga_{1-x}Al_x)_3Si_2O_{14}$ (CTGAS) (x = 0–1) single crystals are of particular interest owing to their relatively high resistivity (more than two orders of magnitude higher than that of LTGA at 400 °C) and excellent piezoelectric properties [12,16,17]. Furthermore, we have demonstrated that the properties of CTGAS vary gradually from

---

[*] Corresponding author.
E-mail address: fu.xiuwei@nims.go.jp (X. Fu).

https://doi.org/10.1016/j.jcrysgro.2018.08.030
Received 5 June 2018; Received in revised form 1 August 2018; Accepted 28 August 2018

Table 1
Reported growths of CTAS single crystals. The defects are identified as: (1) Cracks, (2) inclusion, (3) color center, (4) secondary phases.

No.	Method	Diameter (mm)	Defects	Reference
1	Cz	18	(1), (2), (3)	[18]
2	Cz	~30	(2), (3)	[19,20]
3	μ-pulling down	4–5	(1), (2), (3), (4)	[21]
4	Cz	24	(1), (2)	[22]

$Ca_3TaGa_3Si_2O_{14}$ (CTGS) to $Ca_3TaAl_3Si_2O_{14}$ (CTAS), obtaining the highest piezoelectric and resistivity values for the fully Al-substituted CTAS [17]. However, in spite of the better performance and low-cost perspective (Al is abundant and cheap compared to Ga), the growth of inclusion- and crack-free CTAS single crystals is still a remaining issue that needs to be addressed for practical industrial implementation. It is well-known that the amount of defects in CTGAS rises with the Al increase. Table 1 lists the published works on the growth of CTAS single crystals, including method, size and defects observed. As can be seen, all these reported CTAS crystals present visual defects, in spite of their relative small sizes. On the other hand, the investigation of the electro-elastic properties of CTAS in a wide temperature range is necessary for device fabrication. However, to date there are no reports on the full matrix elements as a function of temperature.

The purpose of this work is to develop high-quality large-size CTAS single crystals. Additionally, the temperature dependence of the electro-elastic coefficients of CTAS is investigated from room temperature (RT) to 650 °C. In the first part, we present the growth of bulk CTAS single crystals through the Cz method. High quality single crystals (up to 2-in. in width) were successfully achieved. In the second part, the dielectric, elastic and piezoelectric properties of CTAS are systematically studied as a function of temperature.

2. Experimental section

2.1. Polycrystalline synthesis and crystal growth

CTAS single crystals were grown by the Cz technique using a 30 kW RF generator. Stoichiometric ratios of 4N purity $CaCO_3$ (Furuuchi Chemical CO.), Ta_2O_5 (H.C. Starck GmbH), Al_2O_3 (Kojundo Chemical Laboratory CO., LTD) and SiO_2 (Furuuchi Chemical CO.) were weighed. After mixing, the raw materials were pressed at 300 MPa, and then sintered at 1250 °C for 20 h. The obtained polycrystalline CTAS ceramics were loaded into Pt crucibles, melted and kept at around its melting point for several hours before seeding in order to homogenize the melt. Afterwards, CTAS single crystals were pulled up using *a*-oriented CTGS/CTAS seeds under $N_2 + 1\%O_2$ atmosphere. The rotation rate and pulling speed were fixed at 12 rpm and 0.5 mm/h, respectively, from the seeding to final crystal separation.

2.2. Characterization techniques

Single crystal X-ray diffraction analysis was carried out at RT using a Rigaku VariMax Saturn diffractometer equipped with a Mo Kα radiation (λ = 0.71073 Å) and CCD detector. A submillimeter-size single crystal was fixed on a thin glass fiber. The collected data were refined and reduced with the Rigaku suite CrystalClear (*d*trek* program package). The structure was solved using the dual-space algorithm method (SHELXT) and refined by the full-matrix least squares on F^2 using SHELXL-2014/7 in the WinGX program package [23,24]. X-ray rocking curve (XRC) analysis was performed on a polished *c*-cut CTAS plate using a PANalytical X'Pert MRD diffractometer equipped with a Cu Kα1 target (λ = 1.54059 Å) and a hybrid two-bounce Ge (2 2 0) monochromator. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on a BRUKER TG-DTA2000SA analyzer. A small piece of CTAS single crystal was grinded into powder, placed in an alumina crucible, and heated at a rate of 10 °C/min from RT to 1500 °C under a reducing gas flow of Ar + 4%H_2. The dielectric, elastic and piezoelectric parameters were determined by the resonance method using an Agilent 4294A impedance analyzer. The samples were cut based on the IEEE standards on Piezoelectricity [25], as shown in detail in Table 2.

Table 2
CTAS specimens for dielectric, elastic and piezoelectric parameters.

Specimens	Dimensions (mm^3)	Vibration mode	Related coefficients
Y-cut plate	5 × 5 × 0.5	–	ε_{11}
Z-cut plate	5 × 5 × 0.5	–	ε_{33}
XY plate	10 × 0.5 × 2	Length extension	d_{11}, s_{11}
YX plate	10 × 0.5 × 2	Thickness/face shear	s_{12}, s_{44}
(*XYt*) + 30° plate	10 × 0.5 × 2	Length extension	
(*XYt*) + 15° plate	10 × 0.5 × 2	Length extension	d_{14}
(*XYt*) − 15° plate	10 × 0.5 × 2	Length extension	s_{13}, s_{14}, s_{33}
(*XYt*) − 30° plate	10 × 0.5 × 2	Length extension	

3. Results and discussion

3.1. Crystal growth

Preliminary growth attempts of CTAS evidenced the difficulties to pull up a single crystal, obtaining instead polycrystalline bulk ceramics as the one shown in Fig. 1(a). Trial-and-error experiments indicated that the crystallinity can be improved by using *a*-oriented seeds [26]. As seen in Fig. 1(b) and (c), this orientation favors a strong faceted plate habit, with large high-crystalline quality transparent regions. At this stage, when the *a*-oriented seed was prepared from the isomorphic compound CTGS, in the middle of the crystal small inclusions formed, which gradually extended till the bottom of the crystal became completely polycrystalline. On the contrary, when the *a*-oriented seed was prepared from a CTAS crystal, the inclusions could be avoided, but instead the as-grown crystals cracked severely after several hours at RT (see inset of Fig. 1(c)). Therefore, the lattice mismatch of CTGS favored the formation of lattice defects and inclusions that could release crystal stressed. Consequently, as a next step in order to suppress the built up stress inside the grown crystals, the temperature gradient in the hot zone was significantly reduced. In conclusion, the growth under a low temperature gradient using *a*-oriented CTAS seeds is crucial for to grow inclusion- and crack-free CTAS single crystals. On the other hand, post-annealing could be beneficial as-well to prevent the cracking tendency.

High-quality CTAS single crystals could be achieved by creating a low temperature gradient and using *a*-oriented CTAS seed, like the one shown in Fig. 2(a). As-grown crystals are characterized by their plate-like habit, exhibiting very smooth *Y*-cut facets, so that the high transparency and scattering-free nature of the crystals can be ascertained by naked eye without any polishing. To the best of our knowledge, this is the first report about the growth of crack- and inclusion-free CTAS single crystals. Once the growth conditions were stablished, the growth of larger size single crystals was a straight forward scaling issue, attaining high-quality CTAS single crystal of 2 in. in width, as shown in Fig. 2(b). This approach proves the potential of CTAS single crystals for cost-effective industrial growth.

3.2. Crystal structure

Table 3 lists the structure data and refinement of CTAS single crystal. CTAS belongs to the trigonal system with space group *P*321. The unit cell contains one formula unit (*Z* = 1) and the lattice parameters are $a = b = 8.0117(2)$ Å and $c = 4.9109(2)$ Å. The crystal structure of CTAS is visualized in Fig. 3 with projections along the (a) ⟨0 0 1⟩ and (b) ⟨0 1 0⟩ directions. There are four different cationic sites,