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Crystallization of indialite/cordierite glass ceramics for millimeter-wave dielectrics

Hitoshi Ohsato[a,b,*], Jeong-Seog Kim[d], Chae-Il Cheon[d], Isao Kagomiya[c]

[a]Nagoya Industrial Science Research Institute, Department of Research, 2F Noa-Yotsuya Building, 1-13 Yotsuya-dori, Chikusa-ku, Nagoya 464-0819, Japan
[b]Functional Materials Laboratory, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[c]Department of Material Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
[d]Hoseo University, Department of Material Science and Engineering, 165 Sechul-ri, Baebang-myeon, Asan-si, Chungnam 336-795, Republic of Korea

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Abstract

Indialite/cordierite ($Mg_2Al_4Si_5O_{18}$) glass ceramics have been reported to show excellent millimeter-wave dielectric properties of low dielectric constant of 4.7 and high quality factor Qf of $>200{,}000$ GHz when crystallized at the temperature range of 1200–1300 °C. The glass ceramics were crystallized to the intermediate indialite phase at 1200 °C, which phase was then transformed to the stable cordierite phase as crystallization temperature increased. In this paper, the crystallization procedure of the glass with pure cordierite composition was clarified by macro difference thermal analysis (DTA) and X-ray powder diffraction (XRPD) patterns. The crystallization of the glass occurred in two steps above the T_g of 778 °C: the 1st step is the formation of β-quartz solid solutions (s. s.) at 919 °C, and the 2nd step is the transformation from β-quartz s. s. to indialite at 946 °C. As increasing the crystallized temperature, indialite phase converted to cordierite. This phenomenon indicates that indialite is an intermediate phase during the crystallization process from glass to cordierite.

Keywords: D. Glass ceramics; Microwave/millimeterwave dielectrics; Cordierite/indialite; Crystallization procedure

1. Introduction

The Nikkei Electronics (NE) magazine [1] published at 2006 in Japan wrote that millimeter-wave communication began to spread out on a public welfare apparatus. In recent year [2], a millimeter-wave communication has reached the runway for takeoffs from a prediction of many twists and turns. A standard of the millimeter-wave communication by the 60 GHz zone converged to "IEE802.11ad.", because of usage on a public welfare apparatus as Wireless Gigabite (WiGig) which is the biggest data communication speed of 7 Gbit per second, the short communication distance approximately 10 m, and advanced properties such as security, power control etc. The millimeter-wave communication can fly away to sky called the public welfare apparatus.

Non-compressed millimeter-wave wireless communications with high data transfer rate have been developed to support the individual system interface which connects PC peripheral devices and a data bus for HDTV, monitor and projectors. Furthermore, the millimeter-wave communication can be applied to radar for Pre-Crash Safety System.

These systems for millimeter-wave wireless communications require dielectric substrates with high quality factor (Qf), low dielectric constant (ε_r), and near zero temperature coefficient of resonance frequency (TCf) [3]. They also require other physical properties such as high thermal conductivity and low thermal expansion [4]. Millimeter-wave dielectrics are required to have high Qf because the utilizations at high frequency causes high losses, and also low dielectric constants for accuracy control of the fabrication. Since the substrates in a radar system are exposed to a wide range of temperature inside a narrow

*Corresponding author at: Nagoya Industrial Science Research Institute, Department of Research, 2F Noa-Yotsuya Building, 1-13 Yotsuya-dori, Chikusa-ku, Nagoya 464-0819, Japan. Tel.: +81 90 7029 6117; fax: +81 52 802 4070.
E-mail address: ohsato.hitoshi@nitech.ac.jp (H. Ohsato).

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space between the front of the engine room and the radiator, the *TCf* of the substrates should be tuned to near-zero. Ceramics substrates are more superior than resin substrates, because of their high *Qf*, near-zero *TCf*, high thermal conductivity, and low thermal expansion [4,5]. Silicates are suitable for millimeter-wave dielectrics because of their low dielectric constant ε_r and high *Qf* as shown in Table 1. The low ε_r comes from the crystal structure consists of silicon tetrahedron SiO_4 with 50% covalency [6]. Cordierite ($Mg_2Al_4Si_5O_{18}$) is one of the silicates that have good dielectric properties [7], and has two polymorphs such as cordierite and indialite. Cordierite is of low symmetry form: orthorhombic crystal system *Cccm* (No. 66), which has $Si_4Al_2O_{18}$ distorted six-membered tetrahedron rings with ordered SiO_4 and AlO_4 tetrahedra. On the other hand, indialite is of high symmetry form: hexagonal crystal system *P6/mcc* (No. 192), which has disordered $Si_4Al_2O_{18}$ equilateral hexagonal rings. [8] Furthermore, a phase called as μ-cordierite exists, which is *β*-quartz solid solutions (s. s.) precipitated at low temperature [9]. Indialite with high symmetry is intermediate phase crystallized from glass with cordierite composition.

The authors presented indialite/cordierite glass ceramics which has high *Qf* values of $>200{,}000$ GHz, low dielectric constant ε_r of 4.7, and *TCf* of -27 ppm/°C as shown in Fig. 1 [10,11]. The ε_r of this material is the lowest among the silicates as shown in Table 1. Fig. 1(a) shows amount of indialite which were analyzed by the Rietveld method calculated by two phases such as indialite and cordierite. Here, amount of residual % corresponds to cordierite. At 1200 °C, the most of the precipitated phases is indialite, and along with increasing the temperature, amount of indialite decrease and that of cordierite increases. So, judging from Fig. 1(a) and (b), indialite shows high *Qf* than cordierite. This *TCf* value is better than that of other substrates having low dielectric constant of ca. -60 ppm/°C as shown in Table 1.

Table 1
List of high *Q* silicate materials with low dielectric constant.

Name	*Qf* (GHz)	ε_r	*TCf* (ppm/°C)
Forsterite Mg_2SiO_4	270,000	6.8	−65
Willemite Zn_2SiO_4	121,000	6.5	−61
Diopside $CaMgSi_2O_6$	121,381	7.6	−66
Wollastonite $(Ca_{1-x}Sr_x)SiO_3$:$x=0.8$	66,700	6.62	−40
Cordierite $Mg_2Al_4Si_5O_{18}$	59,682	6.14	−26.1
Ni-doped cordierite/indialite	100,000	6.8	−65
Indialite/cordierite glass ceramics	>200,000	4.7	−27

In this paper, the procedures of crystallization from glass with cordierite composition are reported, which are analyzed by differential thermal analysis (DTA), X-ray powder diffraction (XRPD) and the Rietveld method.

2. Experimental procedure

Powder materials with cordierite/indialite $Mg_2Al_4Si_5O_{18}$ composition were prepared by using high purity raw materials: MgO, Al_2O_3 and SiO_2 (>99.9 wt% purity). The powders were ball-milled and calcined for decarboxylation, and were melted at 1550 °C using the elevated furnace and refined for removing small air seeds at 1600 °C in Pt-crucible with 40 cc, and quenched in water. The quenched glass pieces were annealed for relieving the thermal stress at 760 °C for 1 h under the glass transition temperature (T_g) of 778 °C. The T_g was obtained by macro DTA as described later. The glass species were crushed by one dimensional press and planetary ball mill (P-6, Classic Line, FRITSCH JAPAN) using a ZrO_2 vessel with 250 cc and ZrO_2 balls. The grain size was measured by Nano Particle Size Analyzer (SIMADZU, SALD-7100) with ultraviolet laser. Dispersion medium was used 0.2 wt% hexa-meta-phosphate sodium solution. The refractive indices of cordierite and ZrO_2 were used 1.55 and 2.40, respectively. The obtained glass powder was performed to macro DTA with 0.7 cm^3 volume of sample. The two Pt-holders for sample and standard of alumina were set in Kanthal super furnace with $100 \times 100 \times 100$ mm^3 heating space, and the difference of the temperature between sample and standard was measured by Nano Volt/Micro Ohm Meter (34420A, Agilent Technologies, Inc.). Thermo couples (TC) are used K-type and B-type up to 1200 °C and 1600 °C, respectively. The heating rate was 10 °C/min. The DTA peaks were identified by the sample heated by the same heating rate of DTA and quenched from the temperature around DTA peaks. The precipitated phases are identified by XRPD, and the ratios of indialite and cordierite phase were determined by the Rietveld method of Fullprof software by Juan Rodriguez-Carvajal [12] in France. The XRPD patterns are obtained by step scanning: 10 s/step, scan angle 0.02°, 2*θ* 10–90° by monochromatized CuKα

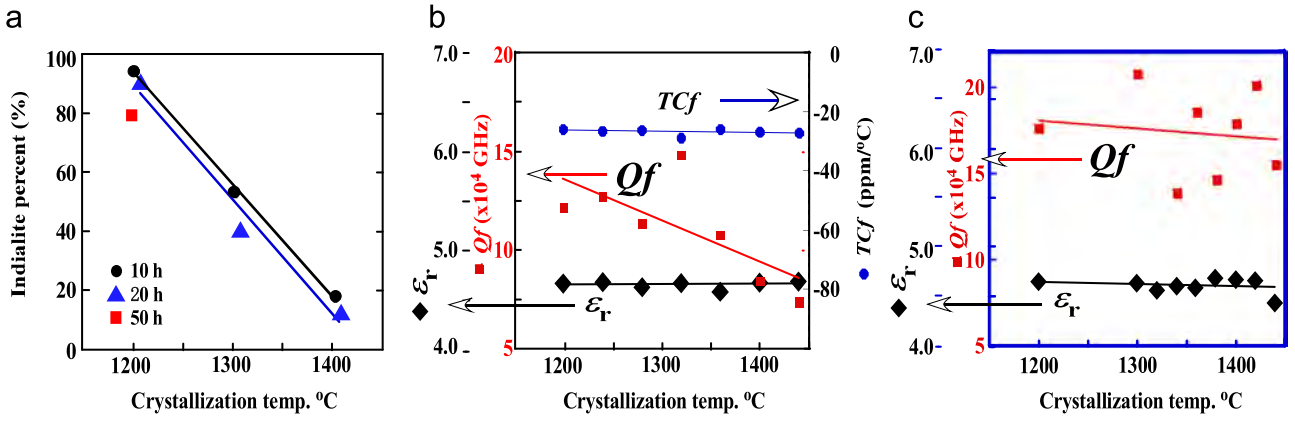

Fig. 1. (a) Amount of indialite, and (b) and (c) millimeter-wave dielectric properties of crystallized at 1200–1400 °C for 10 and 20 h, respectively.

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radiation generated by an X-ray tube 40 KV 20 mA, using Rigaku Rad-C model with a special vertical goniometer.

3. Results and discussion

Grain size of the obtained glass powder was calculated as around 1 μm by the Mie dispersion method using refractive index of 2.40 after milling by using ZrO_2 ball, as shown in Fig. 2(a). When the refractive index of 1.55 for cordierite was applied at first, the distribution pattern of grain size was doubled as shown in Fig. 2(b). The surface of glass powder grains was considered as being coated by ZrO_2 during the planetary ball milling, so the refractive index of 2.40 for ZrO_2 was applied.

Fig. 3 shows two kinds of macro DTA curves of obtained glass powder with cordierite composition. One is high temperature DTA up to 1600 °C using B-type TC as shown in Fig. 3(a), which shows three types of peaks; one is endothermic broad peak around 840 °C, the second one was two exothermic peaks around 900 °C and the third one incongruent melting endothermic peak of 1400 °C. Another one is up to 1200 °C using K-type TC as shown in Fig. 3(b), which shows two type of peaks; one is glass transition (T_g) endothermic peak of 778 °C, and the others are two exothermic peaks of 919 and 946 °C. The T_g was applied to annealing the glass pieces described before.

In order to confirm the crystallization procedure, four small Pt-cells with the glass powder were set in the elevator furnace, and heated to four different temperatures as shown in Fig. 3(b) by the same heating rate as DTA of 10 °C/min. Each sample was taken out at 850, 880, 920 and 950 °C by quickly lowering the sample from the furnace. The XRPD patterns of the samples quenched are shown in Fig. 4. At 850 °C, the sample is still glass phase, at 880 °C, the strongest peak of β-quartz s. s. was appeared [13]. And at 920 °C, β-quartz s. s. were crystallized. The β-quartz s. s. converted to indialite at 950 °C [14–16]. So, the first peak of 919 °C shows crystallization β-quartz s. s. and the second peak of 946 °C indialite. In order to confirm the second DTA peak based on the phase transition from β-quartz s. s to indialite, DTA curve of the β-quartz s. s. crystallized at 870 °C for 10 h was taken. One exothermic peak of 982 °C was appeared as shown in Fig. 5(a), which is same as the second peak of Fig. 3(b). And the XRPD pattern of after DTA was identified as indialite as shown in Fig. 5(b). So, the second peak was appeared by the phase transition of β-quartz s. s. to indialite.

Identification of the glass samples crystallized at 850–1400 °C was performed using XRPD patterns as shown

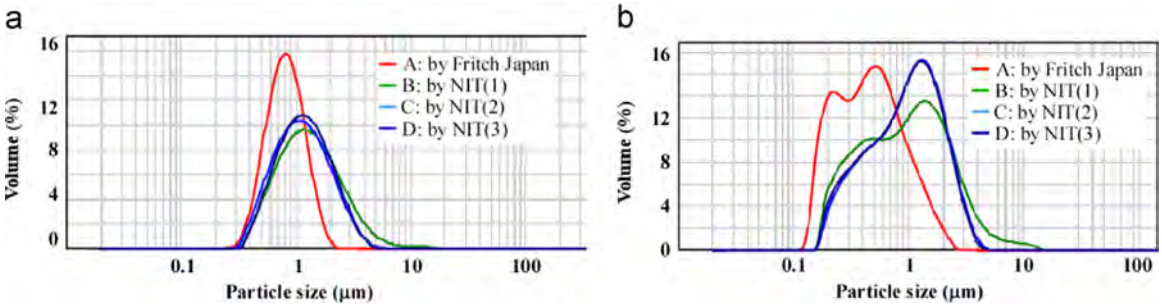

Fig. 2. Grain size of prepared glass powder with cordierite composition measured by Nano Particle Size Analyzer with ultraviolet laser. (a) The data calculated using refractive index of 2.40 for ZrO_2 and (b) 1.55 for cordierite.

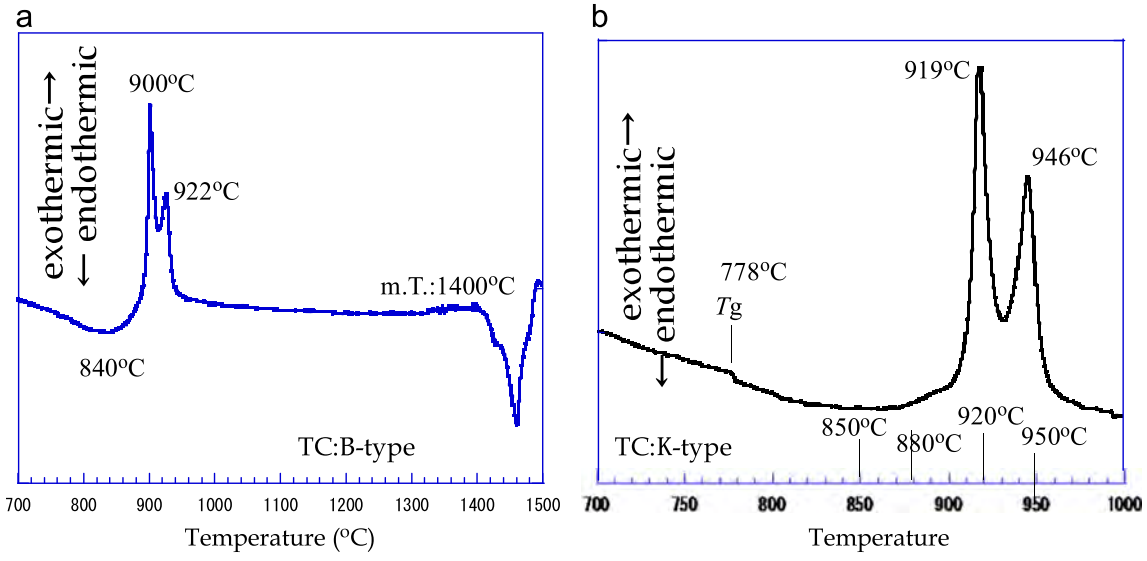

Fig. 3. DTA patterns of prepared glass powder with cordierite composition. (a) High temperature DTA up to 1600 °C using B-type TC. (b) Below 1200 °C using K-type TC.

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in Fig. 6. The samples are crystalized at each temperature for 10 h. Up to the temperature 900 °C, β-quartz s. s. was crystalized, and above 920 °C, indialite was identified. Though β-quartz s. s. is precipitated at the temperature 920 °C as shown in Fig. 4, this sample was crystallized for short time during heating with 10 °C/min. Differences between indialite and cordierite are very hard to recognize, because the XRPD patterns of them are almost same. Miyashiro et al. [17,18] cleared the difference between XRPD patterns of indialite and cordierite as shown in Fig. 7(a) presenting peaks in the range of $2\theta = 28–30^\circ$ for several kinds of samples: synthetic indialite (6), Bokaro indialite (5) and Haddam cordierite (4) for indialite, and Sugama cordierite (3), Laramie Range cordierite (2) and Fe-cordierite (1) in Fig.7(a) for cordierite. The pattern over the range $2\theta = 29–30^\circ$ is most distinctive. Here is only one peak in this range in indialite, while there are at least three peaks A, B and D (as shown in Fig. 7(a)) which are closely spread but clearly distinguishable from one another. Here, the diffractive indexes of A, B and D are 511, 421 and 131, respectively. And the peak C is probably due to the $K\alpha_2$ of refraction 421. Fig. 7(b) shows the refined XRPD patterns of crystallized samples at 920–1400 °C for 10 h analyzed by the Rietveld method using two phases of indialite and cordierite of which atomic coordinates were used in previous paper [11]. Above the temperature 1200 °C, the two peaks become broad, and as increase the temperature, the broadening becomes large. This phenomena is same as the splitting the peak on the cordierite presented by Miyashiro [18] as shown in Fig. 7(a). So, the broadening shows transforming from indialite to cordierite.

The amount of indialite (%) was calculated by the Rietveld analysis as shown in Fig. 8. Two groups by the least square method are shown: one is against all data the 1st line) and another one the 2nd line) is the data above 1100 °C. The 2nd group is similar to that of previous data as shown in Fig. 1(a); indialite transforms to cordierite as increasing the temperature. The amount

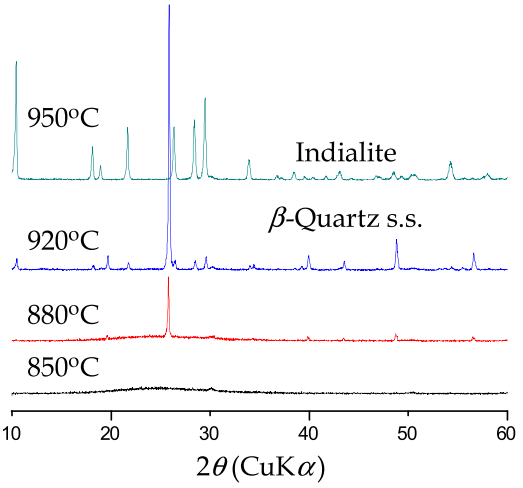

Fig. 4. Precipitated phases for each step around two peaks of DTA. The first peak is crystallized of β-quartz s. s., and the 2nd peak is the transformation from β-quartz s. s. to indialite.

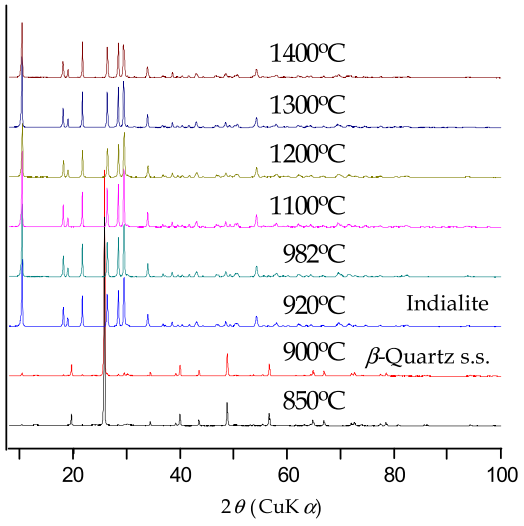

Fig. 6. XRPD patterns of crystallized glass powder at 850–1400 °C for 10 h.

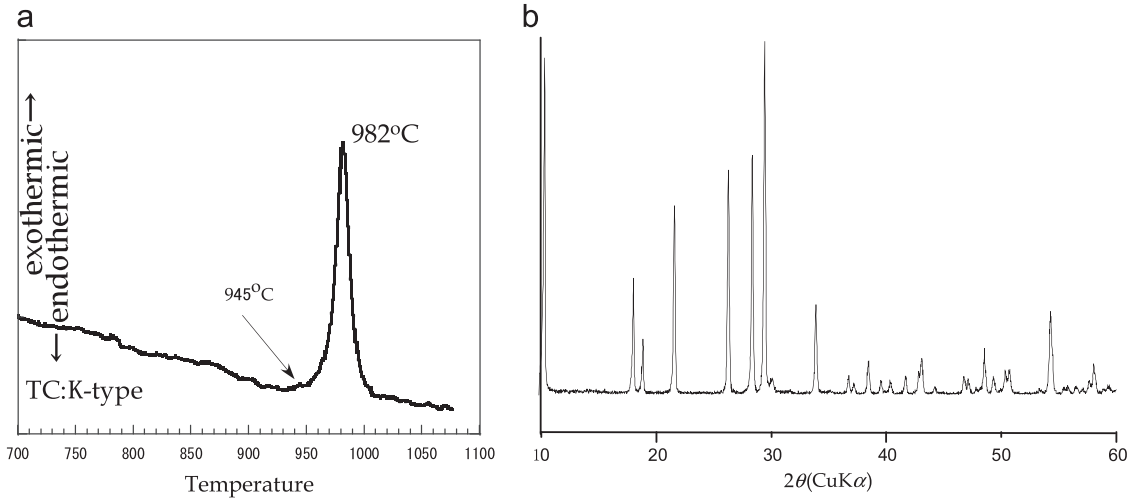

Fig. 5. (a) DTA curve of β-quartz s. s. The peak is only one which transform from β-quartz s. s. to indialite. (b) XRPD pattern obtained after the DTA.

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of indialite is about 90% at 1200 °C, and decrease to 30% at 1400 °C. Based on these phenomena, indialite can be considered as an intermediate phase from glass to cordierite in this temperature area, in which range cordierite is stable. In this area, indialite is metastable phase precipitated from glass phase. Usually, indialite is stated as high temperature phase based on the high symmetry of hexagonal that is disorder form. But the stable region of indialite is actually very narrow or no exist hiding behind of incongruent melting to mullite and liquid phase. Endothermic peak at 1400 °C as shown in Fig. 3(a) is not smooth which might be showing the existence of the order–disorder transition. Three points in Fig. 8 around 900–1000 °C on the 1st line showing around 70% of amount of indialite have been not clarified.

4. Conclusion

The glass powder with cordierite composition is fabricated from the melted glass, and the size was 1 μm measured by the Mie method. And crystallization procedure is studied using macro DTA, identified precipitated phase around two exothermic peaks located between 900 and 950 °C. The glass is crystallized by two

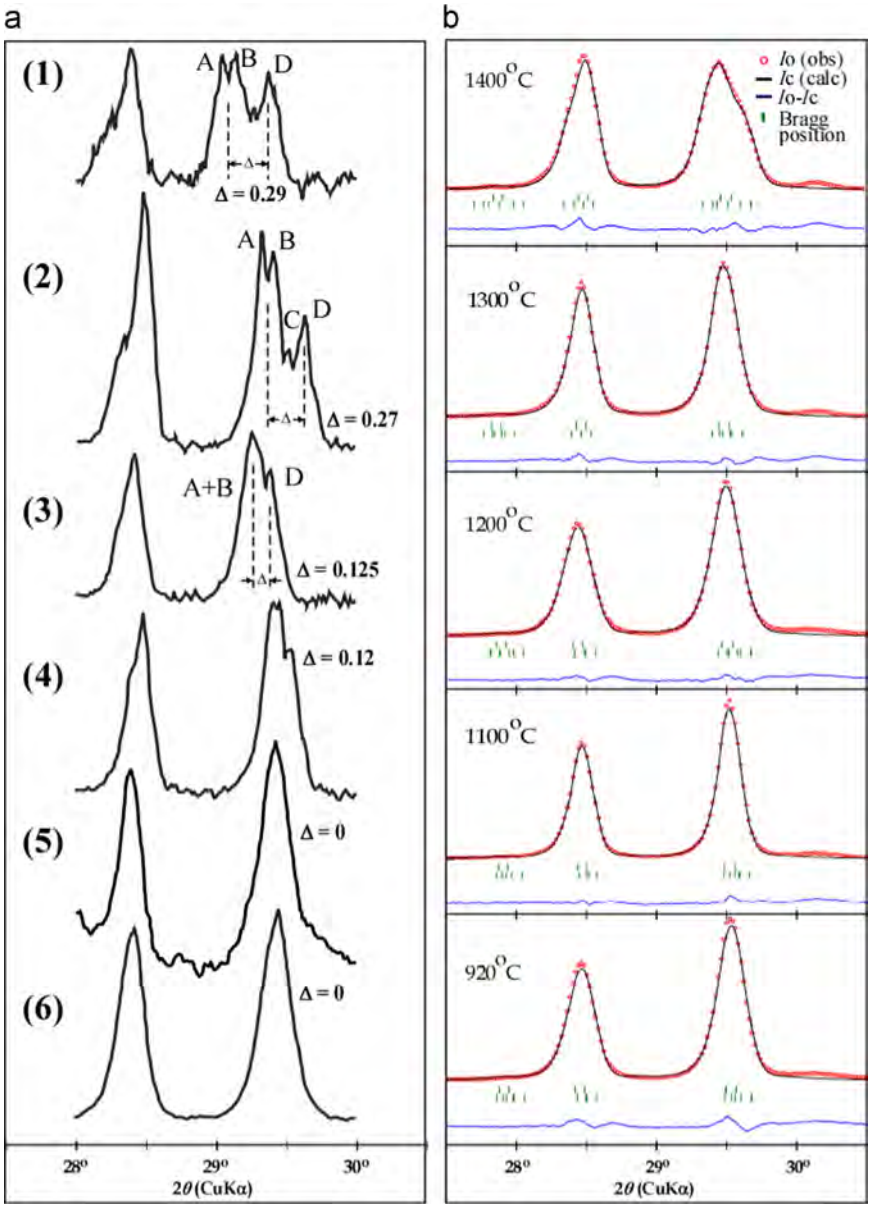

Fig. 7. (a) Difference of indialite and cordierite XRPD patterns between 28° and 30° for 2θ by Miyashiro [18]. The degree of distortion of the cordierite structure is shown by distortion index Δ ($=2\theta_D-(2\theta_A+2\theta_B)/2$). Samples for cordierite: (1) Fe-cordierite, (2) Laramie Range cordierite, (3) Sugama cordierite, and for indialite: (4) Haddam cordierite, (5) Bokaro indialite, and (6) synthetic indialite. (b) Profiles of Rietveld analysis between 28 and 30° for 2θ crystallized at 920–1400 °C for 10 h.

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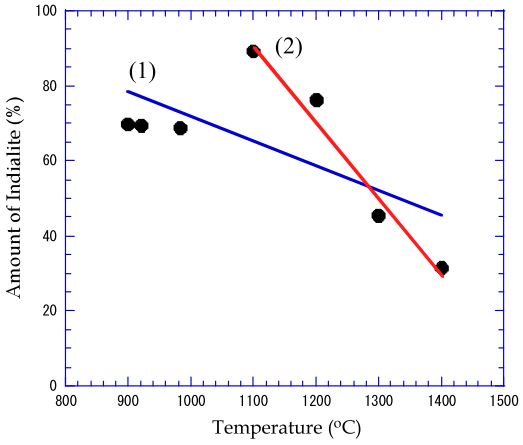

Fig. 8. Amount of indialite in the glass powders crystallized at 920–1400 °C for 10 h. The 1st least square line (1) is for all data, and the 2nd (2) is for above 1100°C.

steps: one is crystallized of β-quartz s. s. at 919 °C, and the second peak is transformation from β-quartz s. s. to indialite at 946 °C. Moreover, based on the XRPD patterns of 920–1400 °C, the differences of the patterns between indialite and cordierite are shown as broadening of peaks between 28° and 30° for 2θ. In this 2θ range, indialite shows only two main peaks. At high temperature of 1200–1400 °C, the broadening of the two peaks is emphasized which shows increasing of cordierite phase. The amount of indialite of crystallized glass above 920 °C is determined by the Rietveld method. There are two groups: one is 900–980 °C and another one is 1100–1400 °C which is similar to previous data. We discussed about indialite as intermediate phase between glass and cordierite.

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