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Crystal growth and the piezoelectric property of the $Ca_3NbGa_3Si_2O_{14}$ compound

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A new piezoelectric $Ca_3NbGa_3Si_2O_{14}$ (CNGS) single crystal was synthesized by a solid state reaction and grown using the Czochralski technique. The crystal structure of the CNGS was found to be isostructural with $La_3Ga_5SiO_{14}$ (LGS). The unit cell parameters were a=0.087 nm and c=0.4989 nm and the space group was P321. The distribution of each cation was found to be ordered in each site. Some piezoelectric properties of CNGS are given.

Key words: $Ca_3NbGa_3Si_2O_{14}$, Czochralski, Structure, Piezoelectric.

Introduction

New compositions isostructural with $La_3Ga_5SiO_{14}$ (LGS) have been studied, and some single crystals of the new compositions showed piezoelectric properties higher than LGS. Such promising findings have led to continuous research in crystal growth of these and other new compositions, and efforts to find improved characteristics continue [1-4].

The LGS crystal belongs to the trigonal system, and has four kinds of cation sites in the structure represented as $A_3BC_3D_2O_{14}$ [5-11]. In this chemical formula, A and B represent a decahedral site coordinated by eight oxygen atoms, and an octahedral site coordinated by six oxygen atoms, respectively. While both C and D represent tetrahedral sites coordinated by four oxygen atoms; the size of the D site is slightly smaller than that of the C site.

In this research, a $Ca_3NbGa_3Si_2O_{14}$ (CNGS) composition was synthesized through a solid state reaction by partially substituting with Ca^{2+} and Nb^{5+} in the A and B sites in $A_3BC_3D_2O_{14}$-type structure. The melting point of the synthesized powder was investigated using differential thermal analysis and grown into a single crystal by the Czochralski method. The linear thermal expansion of the grown crystal was measured along all three axes using a dilatometer. The crystal structure was analyzed by refining the diffraction data of the single crystal using the WinRietveld program. The CNGS crystal's lattice constant gave almost constant values of a=0.085±0.0002 nm along the growth axis.

For application in piezoelectric devices, the quality factor, the electromechanical coupling factor and the piezoelectric modulus of the CNGS crystal were also measured.

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Experimental Procedure

High purity powders ($CaCO_3$, Nb_2O_5, Ga_2O_3, SiO_2) of 4N and above were homogeneously mixed and heated at 1150°C for 12 hours. The synthesized phase was analyzed by powder XRD in the region from 2θ to 60° of its 2θ value. A scan speed was set at 2 degrees/minute and taken at 0.014 degree intervals. Differential thermal analysis (TGD 9700, SINKU-RIKO) was carried out to investigate the melting point of the CNGS composition. The CNGS composition was heated to 1300°C at a heating rate of 10 K/minute.

A single crystal of the CNGS composition was grown by the Czochralski (CZ) method. The furnace used a conventional RF heated CZ furnace with a platinum crucible (50 mm × 50 mm). The growth atmosphere consisted of a mixture of Ar and 2 vol% O_2 gas in order to decrease the evaporation of gallium oxide from the melt during growth. The pulling and crystal rotation rates were 1.0 mm/h and 10 rpm, respectively. The linear thermal expansion of 3 specimens was measured along the x, y and z axis over a temperature range of 25°C to 1000°C using a differential dilatometer (TD5000, Mac science co.), comparing the length difference between a standard and the test sample. The heating rate was 10 K/minute and Al_2O_3 was used as the standard specimen.

The structure analysis of the CNGS crystal was carried out using a single crystal X-ray diffractometer. X-ray data were collected at a scanning speed of 2°/step, from 10° to 110°, at 0.02° intervals.

The WinReitveld program was used for the refinement of the structural parameters. Lattice constants of the CNGS crystal were calculated using the least-square

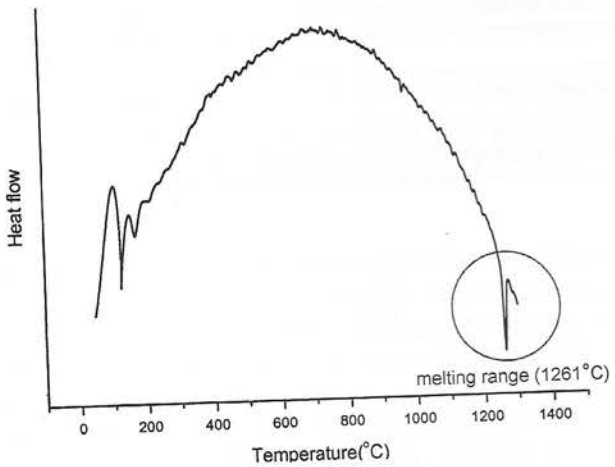

Fig. 1. Differential thermal analysis measured until 1300°C.

Fig. 2. CNGS crystal cut vertical along growth axis.

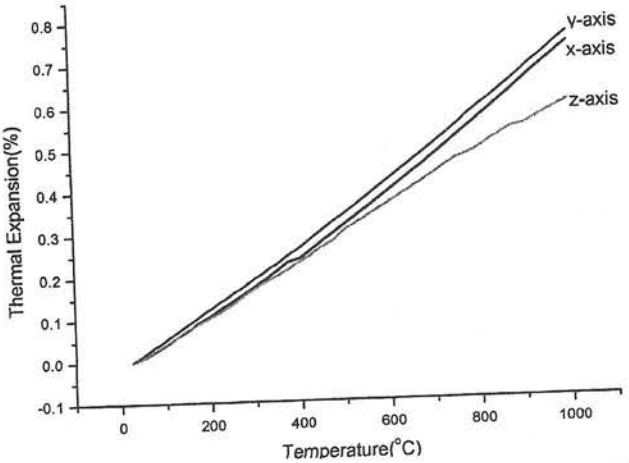

Fig. 3. The linear thermal expansion along x, y and c axis until 1000°C.

method along the growth axis.

To investigate the piezoelectric properties of the CNGS crystal, X-cut resonators of 10 mm × 3 mm × 0.5 mm in dimension were cut and polished. The quality factor, the electromechanical coupling factor and the piezoelectric modulus were evaluated by measuring the dielectric constant and the resonance and anti-resonance frequencies of these resonators in the thickness-longitudinal mode.

Result and Discussion

XRD analysis of the CNGS composition synthesized through a solid state reaction showed the phases present to be isostructural to LGS. DTA results to investigate the melting point are shown in Fig. 1. A marked endothermic reaction occurred at 1261°C, and this temperature was considered to be the melting point of CNGS.

The single crystal was grown by the CZ method. The diameter and length of the CNGS crystal were 21 mm and 120 mm, respectively. It was also partially transparent and used approximately 30% of the initial charge. Figure 2 shows the (001) plane cut vertical to the growth direction.

The linear thermal expansion properties of the 2 specimens measured along the x and y axis showed them to increase at a fixed rate, while the linear thermal expansion property of the specimen measured along the z axis showed it to exhibit a smaller thermal expansion rate than the x, y axes above 600°C. These results are illustrated in Fig. 3, and thermal expansion coefficient ($\alpha_{11} = 7.50\times10^{-6}$/K, $\alpha_{22}=7.73\times10^{-6}$/K, $\alpha_{33}=6.09\times10^{-6}$/K) of specimens along x, y and z axis were obtained.

The crystal structure of CNGS was found to be isostructural with $A_3BC_3D_2O_{14}$. The unit cell parameters were a=0.80873 nm and c=0.49798 nm and the space group was P321. The final R and R_w values for the refinement with anisotropic temperature factors were 0.073 and 0.075, respectively. The converged structural parameters and the selected interatomic distances are given in Table 1 and Table 2, respectively.

The decahedral (3e) site was occupied by Ca, while the octahedral (1a) site was mostly occupied by Nb and partially by Ga, whereas La occupies the decahedral and Ga occupies the octahedral site in the LGS. The occupancies of these atoms were determined to be as follows; Ca=1 at 3e site, Nb:Ga=0.94:0.06 at 1a one, Si=1 at 2d one, Ga=1 at 3f one. These results clearly

Table 1. Atomic parameters of CNGS with estimated standard deviations in parentheses

Atom	Site	x	y	z	B
Ca	3e	0.4299(8)	0	0	1.5730(8)
Nb	1a	0	0	0	0.7473(8)
Ga		0	0	0	0.7473(8)
Si	2d	1/3	2/3	0.4450(9)	0.6130(9)
Ga	3f	0.7440(3)	0	1/2	1.1876(7)
O1	2d	1/3	2/3	0.4450(9)	2.7813(3)
O2	6g	0.4944(1)	0.3220(9)	0.6954(1)	1.8896(2)
O3	6g	0.2387(1)	0.0749(4)	0.2250(1)	0.3317(4)

Table 2. Selected interatomic Distances for CNGS

La polyhedron	Nb octahedron
Ca - O1 × 2 2.614(5)	Nb - O3 × 6 2.044(5)
O2 × 2 2.338(6)	
O2' × 2 2.828(5)	
O3 × 2 2.225(5)	
(Ca-O)av 2.501	

Si tetrahedron	Ga tetrahedron
Si - O1 × 1 1.731(6)	Ga - O2 × 2 1.979(9)
O2 × 3 1.520(6)	O3 × 2 1.958(1)
(Si-O)av 1.626	(Ga-O)av 1.969

indicated that each site was fully occupied by each metal. The distribution of all metals finally determined was $(Ca_3)^{3e}(Nb)^{1a}(Ga_3)^{3f}(Si_2)^{2d}O_{14}$ with the Wyckoff-site notation superscripted. Since this distribution is uncommon among the LGS-type crystals which have been grown thus far, the piezoelectric properties of CNGS crystal were expected to be different from the other LGS-type crystals investigated.

Ca atoms are coordinated to eight O atoms, at distance 0.2225(5)-0.2828(5) nm, forming a distorted cubic antiprism. The average B-O distance (0.2044 nm) is longer than the estimated Nb-O distance (0.2002 nm) and the corresponding one in LNG (2.007 Å). [12-13] The mean Ga-O distance (0.1969 nm) is apparently longer than the mean Si-O distance (0.1626 nm), and the shape of the Ga tetrahedron appears to be more distorted.

Figure 4 shows the lattice parameter variation of the crystal boule grown from the stoichiometric melt composition as a function of the solidified fraction $g = W_{crystal}/W_{initial}$, where $W_{crystal}$ and $W_{initial}$ are the weights of the grown crystal and starting melt, respectively. It was found that the lattice parameter remained almost constant with a value of a=0.8085±0.0002 nm from the

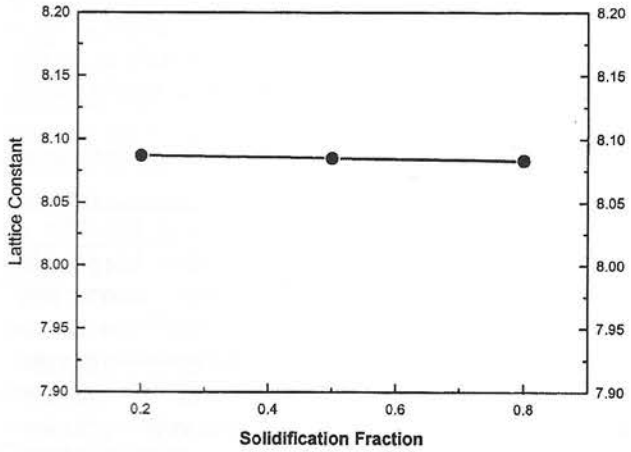

Fig. 4. Lattice constant along the growth direction as a function of solidified fraction, g.

Table 3. Piezoelectric properties of grown CNGS crystal

	LGS [5]	CNGS
Quality factor	30000	56000
Piezoelectric strain constant (d_{11}, 10^{-12}C/N)	-6.16	-7.29
Electromechanical coupling factor (K_{12}, %)	16	18

shoulder to the tail part of the grown crystal. This result suggests that the stoichiometric composition is near to the congruently melting composition of CNGS.

The measured results of CNGS crystal's piezoelectric properties are shown in Table 3. The quality factor, the electromechanical coupling factor (K_{12}) and the piezoelectric modulus (d_{11}) of the CNGS crystal were higher than those of LGS. It was assumed that the high quality factor will have a lower elastic loss and a high electromechanical coupling factor, while the piezoelectric modulus will result in an improved piezoelectric property compared with LGS.

Conclusions

A CNGS compound synthesized by a solid state reaction was grown into a uniform single crystal along the [001] direction using the CZ method. A structural analysis of the CNGS crystal was carried out using the single crystal XRD. In this structural analysis, it was assumed that the CNGS crystal obtained through the partial substitution of Ca, Nb formed a stable $A_3BC_3D_2O_{14}$ structure.

The lattice parameters measured along the growth direction indicated that the CNGS crystal retained the stoichiometric composition from the shoulder to tail.

The quality factor, the electromechanical coupling factor (K_{12}) and the piezoelectric modulus (d_{11}) of the CNGS crystal were found to be higher than those of LGS.

Acknowledgements

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