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SYNTHESIS OF $NdAl_3(BO_3)_4$ CRYSTALS FROM HIGH-TEMPERATURE SOLUTIONS

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By slow cooling method $NdAl_3(BO_3)_4$ crystals were grown from the high-temperature solutions of the five-component system Nd_2O_3-Al_2O_3-B_2O_3-K_2CO_3-MoO_3 where Nd_2O_3 and B_2O_3 were contained in excess of the stoichiometric composition. The grown crystal with hexagonal rod shape were up to 6x1x1 mm in size, bluish purple in color and transparent.

$NdAl_3(BO_3)_4$, abbreviated as NAB hereafter, crystals have been reported to be rhombohedral with space group R32[1-3] and cell parameters a=9.4516 Å, c=7.3066 Å.[3] In the structure of NAB, O atoms form a trigonal prism around each Nd atom, and the Nd-Nd distance is 5.917 Å.[3]

Nd-stoichiometric laser materials, e.g. $LiNdP_4O_{12}$[4] and NdP_5O_{14}[5] , have very low fluorescence quenching despite high Nd concentration. In the same way, it is expected that NAB should be a promising efficient Nd laser material.[3,6-10]

Some attempts have been made to synthesize NAB crystals from the high-temperature solutions using the binary system K_2SO_4-$3MoO_3$[3,11] BaO-B_2O_3 or $BaCO_3$-B_2O_3[8] and the pseudo-ternary system $K_2Mo_3O_{10}$-Nd_2O_3-B_2O_3[12] as fluxes. In addition, the epitaxial layers of NAB were also grown by liquid phase epitaxy.[9] In the former cases,[3,8,11,12] the crystal growth was poorly reproducible,[11,12] and only small crystals(0.5 mm,[3] 1.5 mm[8]) were grown.

The main aim of the present study is to find out the reproducible optimum growth conditions of NAB crystals from the high-temperature solutions of the five-component system Nd_2O_3-Al_2O_3-B_2O_3-K_2CO_3-MoO_3.

The purity of Nd_2O_3 used was 99.9 %, and the other reagents(Al_2O_3, B_2O_3, K_2CO_3 and MoO_3) were the reagent grade ones. Hereupon, the molar ratio of $[K_2CO_3]/[MoO_3]$ in batch compositions was kept 1/3 in all experiments. The batch(about 40 g) was put into a 30 cm^3 platinum crucible. The crucible was placed in an electric muffle furnace.

The temperature conditions for the crystal growth were as follows;

Soaking temperature : 1150°C
Soaking period : 10 hours
Cooling rate : 5°C/hr
Cooling range : 1150-500°C.

After each run, the crystal products were separated from the solidified fluxed melts with hot water.

Table 1 represents the starting compositions, yields and sizes of the produced NAB crystals. Excluding the losses of CO_2 gas, the losses of fluxed melts in these

Table 1 Starting compositions, yields and sizes of produced $NdAl_3(BO_3)_4$ crystals

Run No.	Starting composition					$NdAl_3(BO_3)_4$ crystal		
	Nd_2O_3 (mol%)	Al_2O_3 (mol%)	B_2O_3 (mol%)	K_2CO_3 (mol%)	MoO_3 (mol%)	Yield (g)	[(%)][13]	Max. size (mm)
18	7.9	8.3	28.6	13.8	41.4	0.3	[4]	4x1x1
20	9.1	8.8	20.9	15.3	45.9	0.9	[12]	4x1x1
23	10.4	8.6	28.2	13.2	39.6	3.5	[45]	6x1x1
26	12.1	9.2	18.3	15.1	45.3	1.1	[15]	3x1x1
28	12.5	8.4	40.3	9.7	29.1	0.6	[7]	2x1x1
31	15.0	9.2	28.2	11.9	35.7	1.9	[25]	6x1x1
33	17.1	9.1	35.8	9.5	28.5	0.3	[4]	2x1x1

growth experiments due to evaporation at high-temperature were about 2-8 % in weight at the ends of each run, suggested that the evaporation of fluxed melts had an influence upon the sizes of crystals.

Taking Run No.23 as an example, the schematic illustration of grown crystals in crucible is shown in Fig.1. Hexagonal transparent rod crystals, which were bluish purple in color and up to 6x1x1 mm in size, were mainly grown at the surface of fluxed melt. Some of the crystals were attached to the bottom or wall of the crucible. In general, the crystals grown at the surface of fluxed melt were bigger than the others. This is attributed to the evaporation of fluxed melt. On the other hand, bulky translucent crystals up to 2 mm in size, which were bounded by rough faces and reddish purple in color, were also found mainly at the central part of fluxed melt.

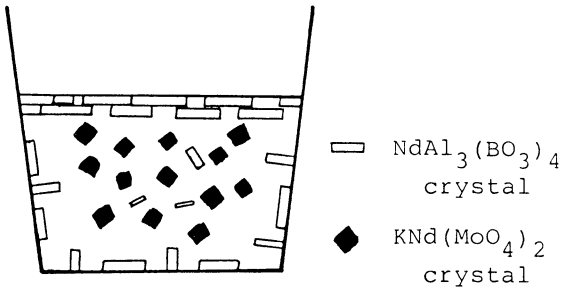


Fig.1 Schematic illustration of grown crystals in crucible (Run No.23)

The hexagonal transparent rod crystals and the coexisting crystals were identified as NAB and $KNd(MoO_4)_2$ by comparison of their X-ray powder patterns with the published data.[1,14]

As seen in Table 1, NAB crystals were only grown from the batches containing the solute components(Nd_2O_3 and B_2O_3) in excess of the stoichiometry of NAB(Nd_2O_3:Al_2O_3:B_2O_3=1:3:4 in molar ratio). Therefore, in these high-temperature solutions, the pseudo-ternary system $K_2Mo_3O_{10}$-Nd_2O_3-B_2O_3 acts as a suitable flux to the growth of the crystal, although the details of this role are not clarified yet.

Judging from the yields and sizes of NAB crystals, the optimum compositions for the crystal growth was of Run No.23, that is, NAB(13.4 mol%)-$K_2Mo_3O_{10}$(30.3 mol%)-Nd_2O_3(17.3 mol%)-B_2O_3(39.0 mol%).

On the contrary, the synthesis of NAB crystals using the batch of the composition written by Ballman[Nd_2O_3(5.5 mol%)-Al_2O_3(16.7 mol%)-B_2O_3(22.2 mol%)-K_2SO_4(13.9 mol%)-MoO_3(41.7 mol%)][11] was unsuccessful in analogy with the same attempt by Hong et al.[3]

As shown in Fig.1, in the respective growth experiments, the coexisting $KNd(MoO_4)_2$ crystals were grown in greater or lesser degree as a result of compound formation between Nd_2O_3, K_2O and MoO_3 in the high-temperature solutions.

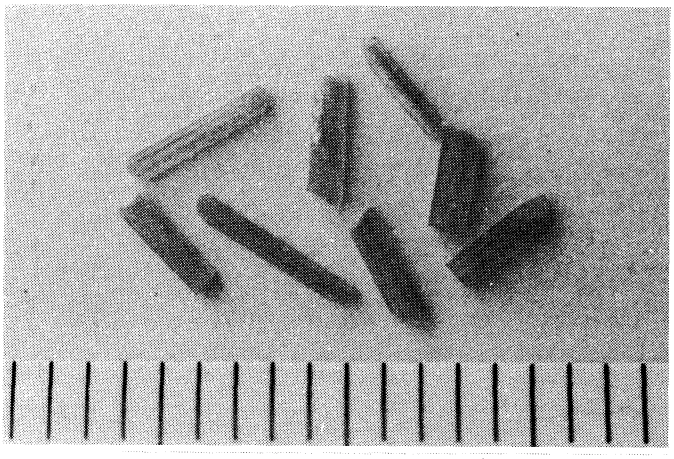
These experimental results described above were reproducible.

An example of grown NAB crystals is shown in Fig.2. These hexagonal crystals were elongated along c axis. According to the observation under a microscope, no visible inclusions were found in these crystals

Density pycnometrically determined was 4.15±0.02 g/cm^3, and almost agreed with the literature one (4.161 g/cm^3).[1] From the density, the number of Nd ion in NAB was estimated to be 5.4×10^{21}/cm^3. This number is about 24 % higher than that(4.37×10^{21}/cm^3)[15] in $LiNdP_4O_{12}$ and about 37 % higher than that (3.96×10^{21}/cm^3)[15] in NdP_5O_{14}.

As seen in Fig.3, DTA curve (heating rate:10°C/min) of NAB crystal shows an endothermic peak at about 1100°C. On the other hand, it was also observed that NAB crystal did not melt at 1200°C, although an opaqueness of the crystal developed at this temperature without changing the crystal shape. From these experimental results, NAB crystal received some thermal change at 1100°C, although it did not melt congruently. However, neither the detailed study on heating process by which the crystal was changed nor the phase diagram of the ternary system Nd_2O_3-Al_2O_3-B_2O_3 or of the pseudo-four-component system NAB-$K_2Mo_3O_{10}$-Nd_2O_3-B_2O_3 was reported yet.

For the crystal growth of NAB, high-temperature solution technique is more advantageous[16] than the other ones because the crystal seems



(1 div.=1 mm)

Fig.2 $NdAl_3(BO_3)_4$ crystals (Run No.23)

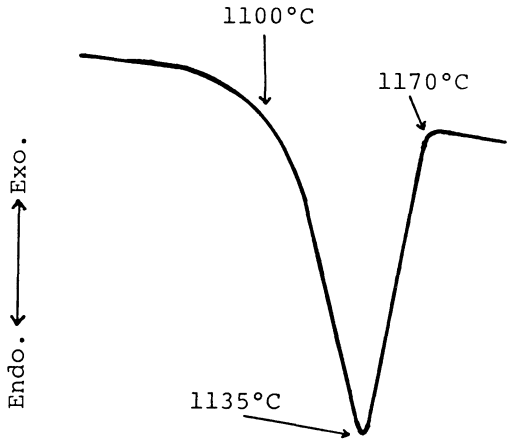


Fig.3 DTA curve of $NdAl_3(BO_3)_4$ crystal

to melt incongruently.

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