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CRYSTAL GROWTH OF $Na(La,Nd)(WO_4)_2$ SOLID SOLUTION FROM HIGH-TEMPERATURE SOLUTIONS

Shuji OISHI and Isao TATE
Department of Industrial Chemistry, Faculty of Engineering,
Shinshu University; Wakasato, Nagano 380

$Na(La,Nd)(WO_4)_2$ solid solution crystals were grown from high-temperature solutions of La_2O_3-Nd_2O_3-WO_3-Na_2CO_3 by slow cooling. These crystals were tetragonal, up to 4-5 mm in size, red purple and mostly transparent. The lengths of a and c axes were considered to obey Vegard's law. This experimental result indicated that the complete series of solid solution isostructural with the end member crystals were obtained.

$Na(La,Nd)(WO_4)_2$ solid solution crystals are expected as one of forthcoming laser materials.[1] Although various kinds of solid solution crystals of sodium rare earth tungstates were already synthesized,[2] the crystal growth of $Na(La,Nd)(WO_4)_2$ solid solution from high-temperature solutions has not been reported as yet.

The authors previously reported the crystal growth and some properties of both $NaLn(WO_4)_2$(Ln=La and Nd)[3] crystals which corresponded to the end members of $Na(La,Nd)(WO_4)_2$ solid solution.

The main purposes of this study were to grow $Na(La,Nd)(WO_4)_2$ solid solution crystals from high-temperature solutions of La_2O_3-Nd_2O_3-WO_3-Na_2CO_3 and to investigate some properties of these crystals obtained.

The chemicals used as starting materials were La_2O_3(99.99%), Nd_2O_3(99.9%), WO_3(reagent grade) and Na_2CO_3(reagent grade). The compositions of batches were as follows.

La_2O_3[(5-x)mol%]-Nd_2O_3[x mol%]-WO_3[65 mol%]-Na_2CO_3[30 mol%]

where x was 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5.

These compositions were chosen with reference to the optimum ones for crystal growth of the end member crystals.[3] The batch(41-45 g) was put into a 30 cm^3 platinum crucible. The temperature conditions for crystal growth were as follows.[3]

Soaking temperature : 1150°C, Soaking period : 10 hours

Cooling rate : 5°C/hr, Cooling range : 1150-500°C

The crystal products were separated from the solidified fluxes with hot water.

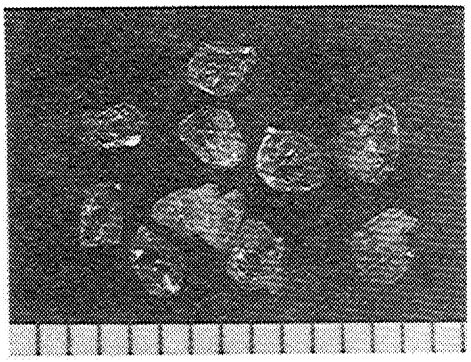
In the growth experiments, the evaporation losses of high-temperature solutions were less than 2 % in weight at the end of each run. As was the case that scarcely any evaporation loss was found, the evaporation didn't seem to produce a powerful effect on the crystallization. Grown crystals were mainly attached to the bottom or wall of the crucible. As an example, these crystals are shown in Fig.1. As previously reported,[3] the colors of $NaLn(WO_4)_2$ crystals were colorless for La and red purple for Nd, respectively. The colors of grown crystals were red purple and had a tendency to turn deeper as the value of x in batch increased. These crystals, whose maximum sizes at respective runs reached 4-5 mm regardless of the difference of x, were mostly trans-

parent. As previously reported,[3] the shapes of end member crystals were octahedron consisting of {101} faces or decahedron consisting of {101} and {001} faces. Although the grown crystals were not bounded by flat faces in almost cases, their shapes seemed to be basically similar to those of the end member crystals.

On the basis of X-ray powder diffraction patterns, these crystals were tetragonal scheelite structure.

The respective peaks in these patterns shifted slightly to the high angle side with increasing x.

The observed lattice parameters(a and c) plotted versus x are shown in Fig.2. The lengths of both a and c axes show an almost linear dependence on x. Approximately this result is considered to obey Vegard's law. The densities pycnometrically determined at 20.0 ±0.5°C increased linearly, as shown in Fig.3, with increasing x. These densities were in good agreement with the ones calculated by using lattice parameters. Further, the melting points measured by using DTA curves, which were given in Fig.4 as an example, at a heating rate of 10°C/min were raised from 1215±5 to 1235±5°C with increasing x. These results seemed to indicate that the complete series of $Na(La,Nd)(WO_4)_2$ solid solution isostructural with the end member crystals were obtained.



(1 div.=1 mm)

Fig.1 Grown crystals from high-temperature solution(x=1)

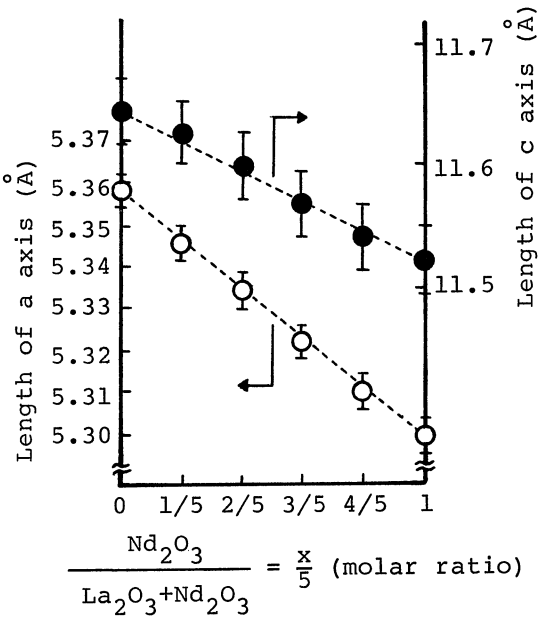


Fig.2 Relation between lattice parameters and x

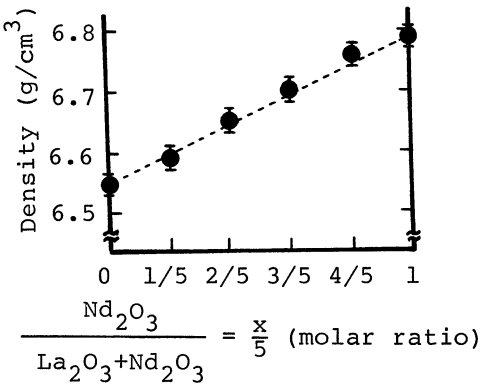


Fig.3 Relation between density and x

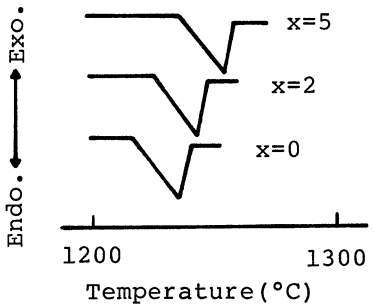


Fig.4 DTA curves of grown crystals

References

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2) For example, L.G. Van Uitert,S.Iida, J.Chem.Phys.,37, 986(1962).
3) S.Oishi,H.Yamauchi, I.Tate, Nippon Kagaku Kaishi,1978, 1630.

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