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SOME EFFECTS OF R(R=Li,Na AND K) IONS ON CRYSTAL GROWTH OF $RNd(WO_4)_2$ CRYSTALS FROM TERNARY SYSTEMS Nd_2O_3-WO_3-R_2CO_3

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$RNd(WO_4)_2$(R=Li,Na and K) crystals were grown from high-temperature solutions of ternary systems Nd_2O_3-WO_3-R_2CO_3 by slow cooling. Grown $RNd\cdot(WO_4)_2$(R=Li and K) crystals were generally bigger than $NaNd(WO_4)_2$ crystals. These crystals, whose shapes were octahedron or decahedron, were reddish purple and mostly transparent. Among these tungstate crystals, $NaNd(WO_4)_2$ crystals had the highest melting point of 1235±5°C.

$LiNd(WO_4)_2$,[1] $NaNd(WO_4)_2$[2] and $KNd(WO_4)_2$(high-temperature polymorph)[3] crystals have a common crystal structure which is similar to that of tetragonal scheelite($CaWO_4$) under atmospheric pressure. The low-temperature polymorph of $KNd(WO_4)_2$ crystals belongs to the monoclinic system.[4] These crystals are of physical interest for their optical[5] and magnetic[6] properties.

Some attempts were made to grow these crystals by the flux method(Li,[1] Na[7-9] and K[10]), the solid state reaction(Li,[11] Na[5,12,13] and K[14]) and the other methods.[15] However, a study on the crystal growth of these three kinds of crystals from high-temperature solutions under the same growth conditions has not been reported as yet.

The authors have reported not only the crystal growth of $NaLn(WO_4)_2$(Ln=La,Nd and Gd) crystals from the ternary systems Ln_2O_3-WO_3-Na_2CO_3[16] but also that of $Na(La,Nd)\cdot(WO_4)_2$ solid solution crystals.[17]

The main purpose of the present study is to investigate the effects of R ions on crystal growth of $RNd(WO_4)_2$ crystals. Therefore, both $LiNd(WO_4)_2$ and $KNd(WO_4)_2$ crystals were newly synthesized, and their colors, transparencies, sizes, habits, lattice parameters, densities and melting points were examined in addition to $NaNd(WO_4)_2$ crystals which were previously studied.[16]

The chemicals used for the preparation of starting materials were Nd_2O_3(99.9%), WO_3(reagent grade) and R_2CO_3(reagent grade). The ternary systems were classified into the following three groups.

(i) NWL ternary system : Nd_2O_3-WO_3-Li_2CO_3
(ii) NWN ternary system : Nd_2O_3-WO_3-Na_2CO_3
(iii) NWK ternary system : Nd_2O_3-WO_3-K_2CO_3

The compositions of these ternary systems were chosen with reference to the optimum ones for the crystal growth of $NaNd(WO_4)_2$ crystals.[16]

The batch(52-59 g) was put into a 30 cm^3 platinum crucible. The crucible was placed in an electric muffle furnace. The temperature conditions for crystal growth were as follows.[16]

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

After a run, the crystals were separated from the solidified fluxes with hot water. Table 1 represents Run No., starting compositions and the maximum sizes of grown crystals. Excepting the losses of CO_2 gas, the losses of fluxed melts in these growth experiments due to evaporation at high-temperatures were less than 2 % in weight at the ends of each run. Therefore, it can be considered that there was little effect of evaporation of fluxed melt on the crystallization.

Table 1 Starting compositions and maximum sizes of grown $RNd(WO_4)_2$ crystals

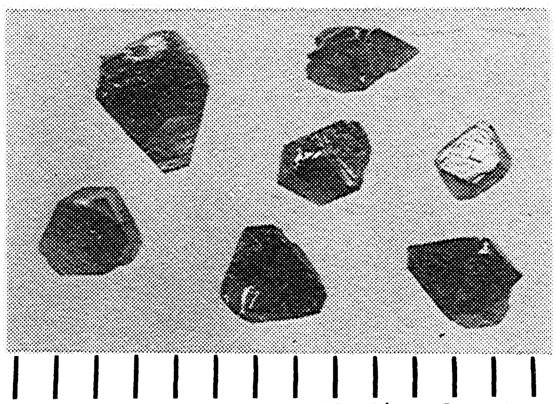
	Run No.	Starting composition (mol%)	Maximum size of crystal (mm)
(i)	NWL-1	$Nd_2O_3(5)$-$WO_3(65)$-$Li_2CO_3(30)$	8x6x5
	NWL-2	$Nd_2O_3(3)$-$WO_3(67)$-$Li_2CO_3(30)$	4x3x3
	NWL-3	$Nd_2O_3(2)$-$WO_3(67)$-$Li_2CO_3(31)$	3x3x2
(ii)	NWN-1	$Nd_2O_3(5)$-$WO_3(65)$-$Na_2CO_3(30)$	4x4x3
	NWN-2	$Nd_2O_3(3)$-$WO_3(67)$-$Na_2CO_3(30)$	4x4x3
	NWN-3	$Nd_2O_3(2)$-$WO_3(67)$-$Na_2CO_3(31)$	3x3x2
(iii)	NWK-1	$Nd_2O_3(5)$-$WO_3(65)$-$K_2CO_3(30)$	8x6x5
	NWK-2	$Nd_2O_3(3)$-$WO_3(67)$-$K_2CO_3(30)$	7x7x6
	NWK-3	$Nd_2O_3(2)$-$WO_3(67)$-$K_2CO_3(31)$	5x3x3

Grown crystals, which were reddish purple, were mainly attached to the bottom or wall of the crucible in each case, regardless of the difference in species of R ions. These crystals were identified by comparison of their X-ray powder patterns with published data of $RNd(WO_4)_2$ crystals (Li[1,11] Na[2,8,12,13] and K[3,10]), respectively. As a result, $KNd(WO_4)_2$ crystals were found to be tetragonal high-temperature polymorph.

As listed in Table 1, grown $RNd(WO_4)_2$(R=Li and K) crystals were generally bigger than $NaNd(WO_4)_2$ crystals. The respective biggest $RNd(WO_4)_2$ crystals were obtained from the batches containing 5 mol% of Nd_2O_3. Therefore, as can be seen from Table 1, NWL-1, NWN-1 and NWK-1 compositions were optimum for the crystal growth of respective $RNd(WO_4)_2$ crystals. On the basis of the assumption that these compositions were pseudobinary systems consisting of solute $RNd(WO_4)_2$- flux $R_2W_xO_y$, the flux compositions were regarded as $R_2W_{1.8}O_{6.4}$. These values($x=1.8$, $y=6.4$) indicate that the flux compositions were not far from $R_2W_2O_7$.

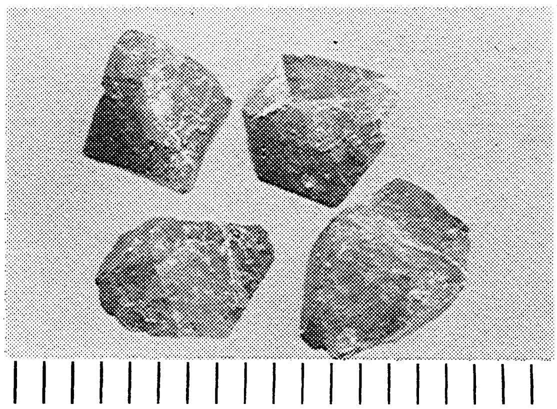
Each example of grown crystals for Li or K is shown in Fig.1 or 2. By measuring the interfacial angles of these crystals, it is shown that the shapes and habits of both $LiNd(WO_4)_2$ and $KNd(WO_4)_2$ crystals are classified into the following two groups in the same manner as with those of $NaNd(WO_4)_2$ crystals.[16]

Octahedron : {101} faces
Decahedron : {101}+{001} faces



(1 div.=1 mm)

Fig.1 $LiNd(WO_4)_2$ crystals (Run No.NWL-2)



(1 div.=1 mm)

Fig.2 $KNd(WO_4)_2$ crystals (Run No.NWK-2)

Table 2 Lattice parameters, unit cell volumes and formula weights of $RNd(WO_4)_2$ crystals

Crystal	Lattice parameter a (Å)	Lattice parameter c (Å)	Unit cell volume ($Å^3$)	Formula weight
$LiNd(WO_4)_2$	5.261±0.004	11.43±0.03	316.4(1.000)	646.9(1.000)
$NaNd(WO_4)_2$	5.300±0.004	11.52±0.03	323.6(1.023[18]))	662.9(1.025[20]))
$KNd(WO_4)_2$	5.372±0.004	11.93±0.03	344.3(1.088[19]))	679.0(1.050[21]))

Therefore, it has been pointed out that the habits of $RNd(WO_4)_2$ crystals don't depend upon the difference of R ions. Regardless of the difference of R ions, a large number of $RNd(WO_4)_2$ crystals were transparent. According to the observation under a microscope, visible inclusions were rarely found in these crystals. However, as for the machinability, $LiNd(WO_4)_2$ and $KNd(WO_4)_2$ crystals seemed to be somewhat more brittle than $NaNd(WO_4)_2$ crystals.

In Table 2, lattice parameters (a and c) observed by using X-ray data, calculated unit cell volumes and formula weights of $RNd(WO_4)_2$ crystals are tabulated. The lattice parameters a and c increased with increase of the ionic radii of R ions in a common tetragonal scheelite structure.

Table 3 Densities and melting points of $RNd(WO_4)_2$ crystals

Crystal	$d_{obs.}$ (g/cm^3)	$d_{cal.}$ (g/cm^3)	mp (°C)
$LiNd(WO_4)_2$	6.83±0.02	6.79	1130±5
$NaNd(WO_4)_2$	6.78±0.02	6.80	1235±5
$KNd(WO_4)_2$	6.55±0.02	6.55	1085±5

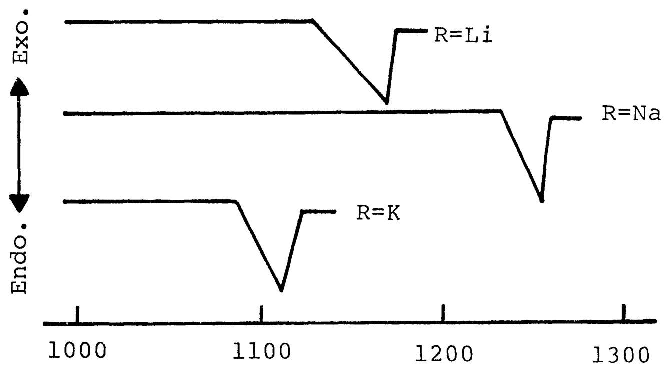


Fig.3 DTA curves of grown $RNd(WO_4)_2$ crystals

Table 3 gives densities, which were pycnometrically determined at 20.0±0.5°C and also calculated by use of lattice parameters, and melting points obtained by use of DTA curves, which were shown in Fig.3, at a heating rate of 10°C/min. The observed densities almost agreed with calculated ones. The density of $LiNd(WO_4)_2$ crystals was nearly equal to that of $NaNd(WO_4)_2$ crystals. This reason seems to be that the increasing ratio[18)] of unit cell volume of $NaNd(WO_4)_2$ crystals is nearly equal to that[20)] of formula weight(see Table 2). On the other hand, the density of $KNd(WO_4)_2$ crystals was smaller than those of the former two crystals. This reason seems to be that the increasing ratio[19)] of unit cell volume of $KNd(WO_4)_2$ crystals is larger than that[21)] of formula weight(see Table 2).

On the basis of the values of densities, the numbers of Nd ion in $RNd(WO_4)_2$ crystals were approximately estimated to be 6.3×10^{21} cm^{-3} for Li, 6.1×10^{21} cm^{-3} for Na and 5.8×10^{21} cm^{-3} for K, respectively.

In these crystals, $NaNd(WO_4)_2$ crystals had the highest melting point of 1235±5°C.

It seems probable that the thermal stabilities of $RNd(WO_4)_2$ crystals are generally changed by both the radii of R ions and their polarizing powers on anionic groups (WO_4^{2-}) when R ions are substituted with one another in the crystal constituents.

So far as these properties(brittleness, melting point and transparency) examined above are concerned, $NaNd(WO_4)_2$ crystals may be one of the best ceramic material in the three kinds of $RNd(WO_4)_2$ crystals.

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17) S.Oishi, I.Tate, Chem.Lett.,1980,1227.
18) The increasing ratio(1.023) is given by [unit cell volume of $NaNd(WO_4)_2$]/ [unit cell volume of $LiNd(WO_4)_2$].
19) The increasing ratio(1.088) is given by [unit cell volume of $KNd(WO_4)_2$]/ [unit cell volume of $LiNd(WO_4)_2$].
20) The increasing ratio(1.025) is given by [formula weight of $NaNd(WO_4)_2$]/ [formula weight of $LiNd(WO_4)_2$].
21) The increasing ratio(1.050) is given by [formula weight of $KNd(WO_4)_2$]/ [formula weight of $LiNd(WO_4)_2$].

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