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Rare-Earth Halides as Fluxes for the Synthesis of Tantalum and Niobium Carbide

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While investigating the reported superconducting phase of $Lu_2Cl_2C_{2-x}$, we discovered a novel synthetic route for making TaC and NbC. TaC and NbC are superconducting refractory carbides with a T_c of 10 and 12 K, respectively. TaC or NbC was initially found as impurity in reactions designed to produce $Lu_2Cl_2C_{2-x}$. TaC and NbC can be prepared as single crystals by reacting Ta or Nb and C in a $LnCl_3$ (Ln = Y, Lu) flux at as low of a temperature as 850 °C for 4 days. The products are characterized by powder X-ray diffraction and magnetic susceptibility. The various conditions for the preparation of the refractory carbides in rare-earth fluxes and their properties will be presented and discussed.

Introduction

Refractory compounds are composed of transition metals in the groups 4, 5, and 6 with nonmetals such as B, C, N, O, Si, P, and S. Transition-metal carbides are especially of interest because they are refractory, possessing properties such as thermal stability, corrosion and wear resistance, and high strength coupled with electronic characteristics such as superconductivity.[1] In recent years, refractory compounds have been used in electronics, electrical engineering, and high-temperature material science. TaC and NbC are added as powder in the manufacturing of hard materials. When used with TaC in hard metals, NbC improves the properties of the sintered material. [1−3] TaC and NbC are resistant to molten metals. Because of their high melting point, TaC and NbC have been used in heating elements of electric resistance furnaces. [4]

Tantalum and niobium carbide have been obtained by the carburization of metal or oxide powders with solid carbon or carbonaceous gases, deposition of carbides from the gas phase, chemical isolation from carburized ferro alloys or molten metals and deposition by fused-salt electrolysis.[5] Industrial production of tantalum carbide is usually carried out by mixing tantalum oxide and carbon at 1750 °C. Niobium carbide is produced by heating the oxide with carbon at 1500 °C. The high temperature required for producing refractory carbides is attributed to the inefficient nature of heat transfer[2] and the high incongruent melting temperature.[2,6] Other methods employed to produce refractory carbides are the use of metallic fluxes[2,7] and the carbothermal reduction of oxides using microwaves.[8] Tantalum carbide can be prepared by reacting tantalum and carbon in molten aluminum and heating the melt to 2000 °C. After cooling, the aluminum is dissolved in acid.[9] The microwave method led to the ability to produce TaC at temperatures as low as 1500 °C.[8] Rapid metathesis reactions as well as solid combustion synthesis are promising routes to refractory ceramics and carbides and have been recently reviewed. [10,11]

Compounds in the $RE_2X_2C_{2-x}$ (RE = Y, La, Lu; X = Cl, Br, I) system have been reported to be superconducting with transition temperatures ranging from 6 to 8 K.[12−14] Of the single halides, $Lu_2Cl_2C_{2-x}$ has the highest reported transition temperature of 8 K. The highest T_c reported to date is 11.2 K for $Y_2I_{1.6}Br_{0.4}C_2$.[14] These compounds crystallize in the 3R structure-type and the carbon is present as C_2^{4-} units.[15] A recent addition includes $La_9Br_5(CBC)_3$ which has a T_c of about 5.5 K.[16] The molecular interstitials are believed to stabilize the metal-rich cluster. The electronic structure has been examined in detail, and superconductivity is attributed to the promotion of effective electron−phonon coupling through the stretching and wagging vibrations of the C_2 unit.[12−14,17] In efforts to better characterize and identify the superconducting phase of $Lu_2Cl_2C_{2-x}$, a series of $Lu_2Cl_2C_x$ $(1.0 < x < 3.0)$ compounds were prepared. These phases were prepared at 1150 °C from the stoichiometric reaction of $LuCl_3$, Lu, and C in a Nb or a Ta tube. The samples showed T_c's consistent with NbC or TaC dependent on the reaction vessel. These results suggest that $Lu_2Cl_2C_{2-x}$ is not an intrinsic superconductor. To further investigate the production

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NbC or TaC, we have examined the reaction conditions using $LuCl_3$ and YCl_3 as a flux. This paper presents the formation of TaC and NbC via a rare earth halide flux that enables the production of crystals in high yield at a lower temperature than conventional routes.

Synthesis

Lutetium ingots (99.9% purity) were purchased from Aldrich. Graphite (99.9%) from AESAR was dried at 200 °C under high vacuum, ground into a very fine powder. Lutetium pieces were cleaned with ethanol and then filed with a carbide file or cut with a diamond saw. Lu metal and C were transferred directly into a nitrogen-filled drybox. $LuCl_3$ and YCl_3 were prepared by the ammonium halide route ($12\ NH_4Cl + Ln_2O_3$).[18] The resulting $(NH_4)_3LnCl_6$ was decomposed to $LnCl_3$ at 360 °C under vacuum (10^{-6} Torr). The $LnCl_3$ was sublimed three times subsequently at 960 °C in vacuo, affording white crystalline $LnCl_3$. Lu_2O_3 and Y_2O_3 (Rhone-Poulenc, 99.995%) and NH_4Cl (Fisher 906586) were starting materials in the ammonium halide route.

$Lu_2Cl_2C_x$ compounds were prepared by heating the mixture of Lu, $LuCl_3$ and graphite ($^1/_3$:$^2/_3$:1 ratio) for 10 days at 1150 °C. The mixture of the materials was placed in a welded tantalum (or niobium) tube in the drybox and sealed with an arc welder under argon atmosphere. The sealed Ta tube was then jacketed in a fused quartz tube under vacuum and loaded into a furnace. The samples were heated at 30 °C/h to 1150 °C for 4−10 days. The samples were cooled to room temperature at a rate of 30 °C/h. Bronze polycrystalline air and moisture-sensitive products were obtained. Samples were initially characterized by powder X-ray diffraction. Majority of the diffraction lines could be fit to a combination of 1T and 3R phases of $Lu_2Cl_2C_x$.[15]

To purposefully produce TaC or NbC in a rare-earth flux, varying amounts of tantalum or niobium and carbon (graphite) were placed in a Ta or Nb tube with excess $LuCl_3$ or YCl_3 (1:1 molar ratio of carbon to YCl_3) and heated for 5 days at 800, 850, and 1000 °C. In addition, stoichiometric mixtures of the elements with YCl_3 in a 1:1 molar ratio of (C: YCl_3) were pressed into a pellet, placed in an alumina boat, and sealed in a quartz ampule under 0.25 atm of argon and heated for 5 days at 900 °C.

Characterization. *X-ray Powder Diffraction.* X-ray powder diffraction data of the products were obtained using an Enraf-Nonius Guinier powder camera equipped with a quartz monochromator that gave clean Cu Kα_1 radiation. Powdered silicon (NBS) was included in the samples as an internal standard, and the positions of the five observed lines were fitted to known diffraction angles by a quadratic function using the program *Guin*.[19] In addition, a Siemens D500 powder diffractometer was used to collect data on several samples.

Magnetic Measurements. Temperature-dependent magnetic susceptibilities were measured with a Quantum Design SQUID magnetometer with an applied field ranging from 1 to 15 G. The data were collected and analyzed with the Magnetic Property Measurement System (MPMS) software supplied by Quantum Design. The samples were prepared by loading 20 to 25 mg of powdered sample into a fused silica tube designed to provide negligible background (approximately 1 mm ID × 2 mm OD) in the drybox. The tube was then sealed under high vacuum (1×10^{-6} Torr).

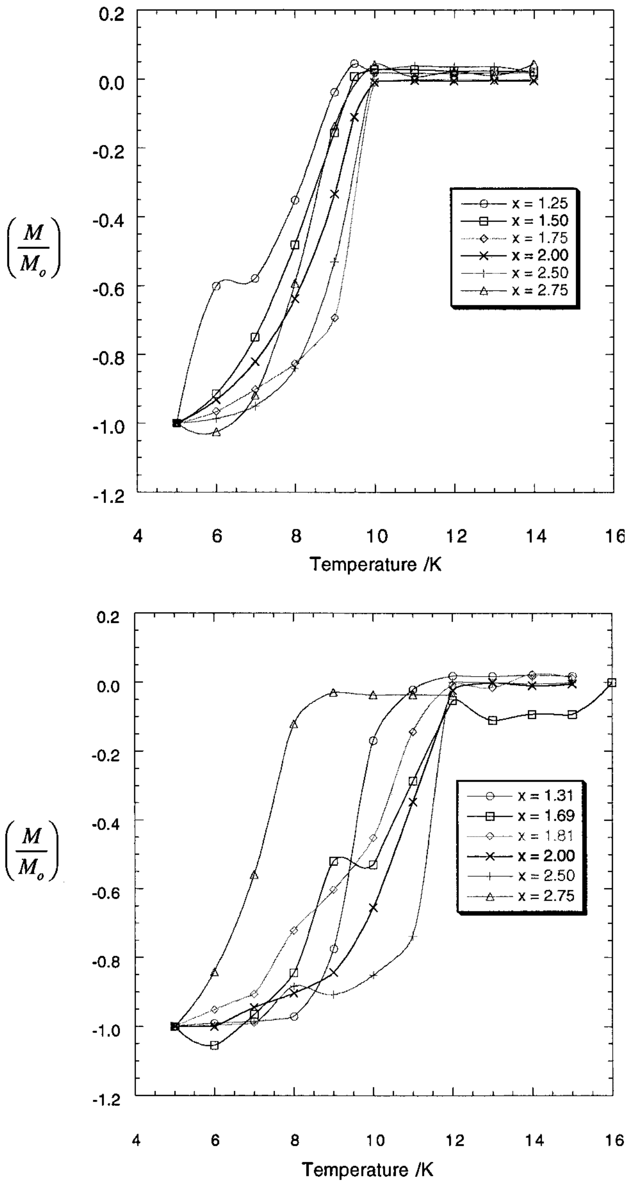

Figure 1. Normalized temperature-dependent magnetization for samples prepared in (a, top) Ta and (b, bottom) Nb tube.

Results and Discussion

Figure 1 shows the normalized temperature-dependent magnetization of $Lu_2Cl_2C_x$ prepared in either a Ta or Nb tube. The most striking aspect of this figure is that the onset of superconductivity is approximately the same for all samples according to whether they were prepared in a Ta or Nb tube, regardless of the amount of carbon, x, used in the syntheses. The stoichiometries listed in the figure correspond to that expected for a stoichiometric product and not an analytically determined quantity. A T_c of 10 K was observed for all samples that were reacted in a Ta and a T_c of 12 K, with the exception of $x = 2.75$, was obtained when the reactions were run in a Nb tube. TaC has a T_c of 10 K and NbC has a T_c of 11−12 K.[20−22] The broadness of the peaks could be attributed to nonstoichiometric Ta or Nb carbide or to the size of the field applied when measuring samples. It has been observed that T_c varies with carbon stoichiometry in TaC_x and NbC_x.[21] The transition temperature, T_c, to the superconducting state for the disordered carbide TaC_x decreases rapidly with the carbon content, being 10.1−1.5 K for $TaC_{1.00}$ to $TaC_{0.83}$, respectively.[20] The values of T_c for niobium carbides in the homogeneity range decrease sharply

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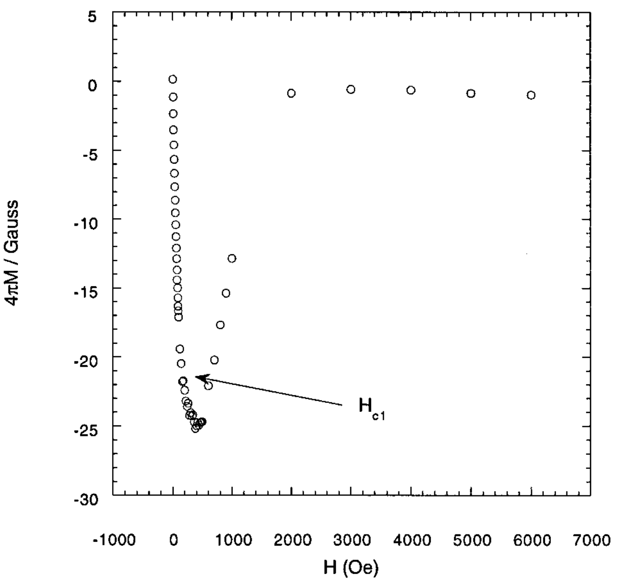

Figure 2. Field-dependent magnetization for $Lu_2Cl_2C_{1.75}$, prepared in a Ta tube. The arrow indicates H_{c1}.

Table 1. Volume Fraction as a Function of x in $Lu_2Cl_2C_x$ for Samples Prepared in Ta or Nb Containers

tantalum		niobium	
x	superconducting volume fraction (%)	x	superconducting volume fraction (%)
1.25	0.22	1.31	1.3
1.50	1.63	1.69	0.1
1.75	25.5	1.75	5.0
2.00	5.3	1.81	0.2
2.25	not superconducting	2.00	14.3
2.50	3.1	2.50	3.3
2.75	0.6	2.75	0.2

from 11−12 K to <2 K for the $NbC_{0.99}$ to $NbC_{0.72}$.[21] This may account for the lower T_c observed for the $x = 2.75$ sample prepared in a Nb tube. Volume fractions for the samples are given in Table 1. Regardless of the amount of carbon, they are all fairly low. In addition, the $x = 2.25$ sample prepared in a tantalum tube showed no superconductivity and $Lu_2Cl_2C_{1.75}$ showed the largest volume fraction of superconductivity.

Field-dependent magnetization was measured for several samples prepared in Ta or Nb tubes in order to obtain more information concerning the identity of the superconducting phase. Figure 2 shows the field dependent magnetization data for the sample with the largest superconducting volume fraction, $Lu_2Cl_2C_{1.75}$. This figure is typical of all the samples prepared in Ta that was measured and shows H_{c1} equal to 212 Oe. Samples prepared in Nb show H_{c1} equal to 75 Oe. Our experimental values are in good agreement with the expected critical field for Ta and Nb carbides that have a critical field of 220 and 100 Oe.[22]

The 3R and the 1T structure of the $Lu_2Cl_2C_{2-x}$ were identified for the samples prepared in either a niobium or tantalum tube which is in agreement with literature.[15] Upon further evaluation, it was found that at least the two strongest diffraction peaks of TaC or NbC were also present in our powder patterns, with the exception of the one sample, $Lu_2Cl_2C_{2.25}$ prepared in Ta, which did not exhibit superconductivity. Table 2 shows the number of TaC or NbC lines identified for each sample prepared.

It is rather surprising that TaC and NbC can be prepared in this reaction. There is no evidence for the formation of TaC or NbC in any other interstitially stabilized rare-earth halide clusters.[13] The condensed $M_6Cl_{12}Z$-type structure with interstitials Z has been extensively investigated for M = Sc, Y, Zr, and Gd.[23] However, there is not very much work on carbon-stabilized Lu halide clusters.[24] Although welded tantalum and niobium containers appear to be suitable for high-temperature synthesis of interstitially stabilized rare-earth halides,[25] $LuCl_3$ apparently dissolves a small amount of the metal. X-ray fluorescence of $LuCl_3$ showed that it was free of Ta or Nb contaminants before the reaction with carbon suggesting that $LuCl_3$ is much more reactive toward Ta or Nb than the rare earths investigated to date. The $x = 2.25$ sample prepared in Ta showed no superconductivity, and there was no evidence for TaC in the powder pattern. Since all samples were prepared in the same fashion, at this time, we have no explanation for why $LuCl_3$ did not react with the Ta container. Obviously, there are other factors that are important. This work shows that $Lu_2Cl_2C_{2-x}$ is not intrinsically superconducting and is in agreement with the extremely small superconducting volume fraction observed in this and Simon's work.[13] Whether or not the rare-earth halide carbides and boro carbides are intrinsic superconductors could be ascertained by heat capacity measurements or if the syntheses of these compounds were carried out in non-carbide-forming containers.[12−14,16]

Direct reaction of Ta or Nb and C was investigated in $LuCl_3$ and YCl_3. YCl_3 flux was chosen because it is a less expensive rare-earth flux. Table 3 provides various temperature schemes, length of reaction times, and flux to carbon molar ratios. Ta or Nb was initially reacted with C and YCl_3 at 1100 °C (Temperature at

Table 2. X-ray Data (Number of Diffraction Peaks) for TaC, Ta_2C or NbC, Nb_2C Observed in $Lu_2Cl_2C_x$

x	TaC	Ta_2C	x	NbC	Nb_2C
1.25	4	3	1.31	2	
1.50	2	2	1.69	1	3
1.75	4	1	1.75	3	
2.00	4	3	1.81		
2.25			2.00	2	2
2.50	4		2.50	3	3
2.75	3		2.75	2	1

Table 3. Reaction Conditions for the Production of TaC/Ta_2C and NbC/Nb_2C[a]

temp (°C)	time	
		TaC/Ta_2C
1150	10 days[b]	50/50
1150	14 days[c]	60/40
1000	10 days[c]	58/42
1000	5 days/2 °C[c]	50/50
1000	5 days/pellet[c]	50/50
1000	4 days/10 °C[c]	40/60
1000	24 hours[c]	40/60
1000	4 days[c]	50/50
800	10 days[c]	40/60
850	10 days[c]	30/70
		NbC
1150	10 days[b]	100
1000	4 days[c]	100

[a] All samples have a stoichiometric ratio of 1:1:1 ratio of Ta:C:YCl_3 unless otherwise indicated. [b] $LuCl_3$. [c] YCl_3.

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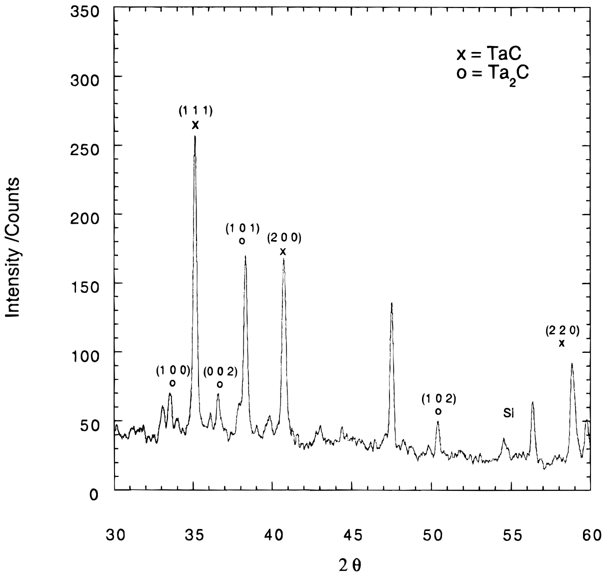

Figure 3. Powder diffractogram of the product of Ta + C at 1100 °C for 10 days. × indicates TaC, and O indicates Ta_2C.

which $Lu_2Cl_2C_x$ reactions were run). Figure 3 shows the powder diffraction pattern of a sample prepared from Ta, C, in a YCl_3 flux at 1150 °C. From powder diffraction, TaC and Ta_2C were identified. TaC can also be prepared directly using YCl_3 or $LuCl_3$, Ta metal, and C at temperatures below 1150 °C. After heating, the samples were washed with water, thus affording TaC crystals. In addition, Ta_2C was also identified from the powder patterns. The best yield was the sample prepared at 1150 °C for 14 days. At 1000 °C, the yield of TaC to Ta_2C was 58:42 estimated from the 100% peaks in the powder diffraction. Because of the tantalum rich environment for this reaction, a ratio of Ta:2C was investigated to see whether TaC could be prepared without Ta_2C. According to the powder pattern, approximately 50:50 of the TaC and Ta_2C was afforded.

Another sample was prepared with the ratio of 1Ta: 10C, and surprisingly with the larger carbon ratio yielded a larger ratio of Ta_2C. When the sample was heated for 24 h at 1000 °C, a ratio of 40:60 TaC:Ta_2C was produced also. To investigate the flux without the container, Ta, C, and YCl_3 were pressed as a pellet and heated in an alumina boat. The ratio of TaC to Ta_2C produced is approximately 50:50. At 850 °C, the yield of TaC is also reasonable but Ta_2C is still obtained. Heating for 10 days at 800 °C also yielded TaC and Ta_2C and some unreacted tantalum. Although heating the samples longer promote a higher yield of TaC, the increase in yield is not significant.

NbC can also be prepared directly by reacting Nb, C, and YCl_3 at 1000 °C. Figure 4 shows the powder diffraction pattern of NbC prepared at 1000 °C for 4 days in a YCl_3 flux. The X-ray diffraction pattern confirms that this compound is NbC with a B1 rock salt structure. Unlike TaC, there is no evidence for Nb_2C, although the diffraction pattern contains two unidentified peaks.

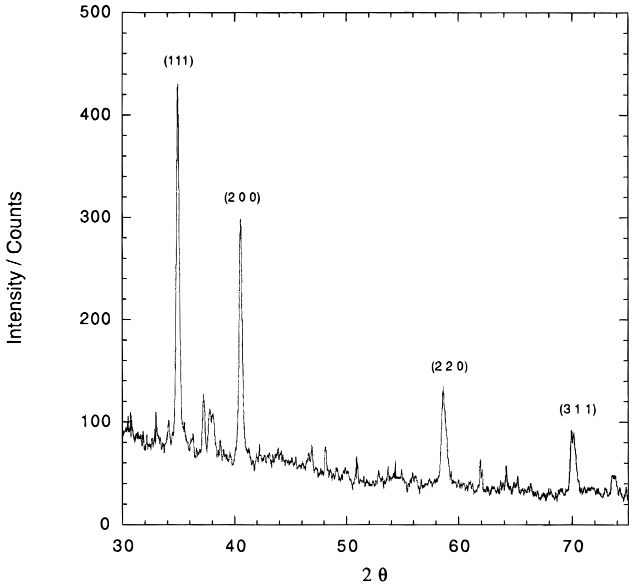

Figure 4. Powder diffractogram of Nb + C at 1000 °C for 4 days. Indexed reflections are for NbC.

Conclusions

Refractory carbides, with their useful properties and processing requirements, continue to challenge the metallurgical community to improve the synthesis. Fluxes and fluxing technology in metallurgical industries are important because they have been employed in processes such as metal extraction, purification, and recycling process.[26] Employing rare-earth fluxes such as YCl_3 or $LuCl_3$ to produce TaC or NbC in high yield at a relatively low temperature is promising. From the results of this investigation, YCl_3 and $LuCl_3$ play an important role in the production of TaC and NbC. The present work complicates the current search for superconducting phases of rare-earth carbide halides, and care should be taken to ensure that the sample is free of TaC_x or NbC_x.[20,21] In the presence of a rare-earth flux, TaC and NbC can be produced at a lower temperature than previously reported.

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