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PREPARATION OF HIGH PURITY LANTHANUM COMPOUNDS FOR USE IN FLUORIDE OPTICAL FIBERS

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ABSTRACT

The preparation of ultra-pure lanthanum nitrate by coprecipitation is described. Preparation of high purity lanthanum carbonate from the pure nitrate is also described. Hydrofluorinationof pure lanthanum carbonate produces high purity lanthanum fluoride used in the preparation of heavy metal fluoride glasses.

MATERIALS INDEX: fluoride, carbonate, nitrate, lanthanum

Introduction

Heavy metal fluoride glass fibers composed of zirconium, barium, lanthanum, aluminum, and sodium fluorides(ZBLAN) have been proposed for ultra-long repeaterless fiber communication links.^{1,2,3,4} Theoretically, the intrinsic loss of such fibers will be 0.01 dB/Km at 2.55 uM^[5], an order of magnitude better than silica fibers. However, the transition elements iron, cobalt, nickel, and copper, as well as the rare earth neodymium absorb in the vicinity of 2.55um causing much higher losses than theoretically predicted.^{6,7} In order to attain the theoretical minimum loss of 0.01 dB/Km, transition element and rare earth impurity concentrations in the individual metal fluorides or the glass must meet those listed in Table 1.

The impurity concentrations shown in Table 1 are calculated using the equation:

$$[imp], ng/g = L/(wt.)a$$
 (1)

where:

[imp] - impurity concentration, ng/g L = 0.0004dB/Km/component/impurity ion wt. % - weight percent of individual component in glass a - absorbtivity of individual impurity ion in glass⁷ [(dB/Km)/(ng/g)]

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TABLE 1

Purity Requirements For ZBLAN Glass Components And Glass

		Impuri	ty C	oncentrat	ion, pg	;/ g*		
<u>Compound</u>		<u>Fe</u>		<u>Co</u>	<u>Ni</u>	-	<u>Cu</u>	<u>N d</u>
ZrF ₄		50		40	310		250	30
BaF ₂		130		120	830		670	90
LaF3		660		580	4100		3300	450
Alfa		1400		1200	8500		6800	1000
NaF		140		120	880		710	100
Glass		130		120	830		660	89
	* -	parts	per	trillion,	, solid	basis		

The constant L is calculated by assuming equal contributions to the total loss from the 5 fluorides and the 5 impurity ions:

 $L = 0.01 \text{ dB/Km} \div 5 \text{ components} \div 5 \text{ impurity ions}$ (2)

Table 1 indicates that the metal fluorides, as well as the glass, must contain low, or sub-part-per-billion concentrations of iron, cobalt, nickel, copper, and neodymium. To achieve such low levels of impurities in either the glass or the metal fluorides, novel purification and analytical techniques must be developed. Much work has been devoted to preparation of high purity zirconium and hafnium fluoride since these are the primary components of the glass.⁸ Little work, however, has been done on the purification of the other four components of the glass. This work describes the purification of lanthanum nitrate via coprecipitation and subsequent preparation of high purity lanthanum carbonate and fluoride from the purified lanthanum nitrate.

<u>Experimental</u>

The lanthanum oxide used was obtained from Ames Laboratory, Ames Iowa. Ammonium carbonate, barium chloride, "Ultrex" ammonium hydroxide and nitric acid were purchased from J.T. Baker Chemical Company. Sub-boiling point distilled hydrofluoric acid was obtained from the National Bureau of Standards⁹. Doubly deionized water was used throughout the processing. All manipulations were done in acid washed standard laboratory glassware in a class 100 clean room. Hydrofluorination was carried out in acid cleaned TFE teflon containers. Analysis of lanthanum nitrate and carbonate solutions were done on a Perkin-Elmer model Zeeman 5100 Graphite Furnace Atomic Absorbtion Spectrophotometer (GFAAS) using palladium and magnesium nitrates as matrix modifiers.¹⁰ Vol. 24, No. 2

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Procedure

1. Purification of the Lanthanum Nitrate Solution

To a beaker containing 100 ml deionized water and 250 ml "Ultrex" nitric acid, 200g(0.61 mole) of lanthanum oxide is slowly added. After complete addition, the solution volume is reduced to 1/3 its original by boiling, forming a viscous liquid which solidifies if left to cool. A solution of approximately 3M lanthanum nitrate is prepared by addition of 200ml of deionized water to the hot lanthanum nitrate solution. The solution is stirred via a mechanical stirrer and the pH adjusted to 6 by addition of "Ultrex" ammonium hydroxide. A precipitate of lanthanum hydroxide is thus formed:

 $La(NO_3)_3(aq) + NH_4OH(aq) \longrightarrow La(NO_3)_3(aq) + La(OH)_3(ppt)$

The precipitate is aged for 24 hours, gravity filtered through a Whatman #42 filter paper, and the filtrate collected in a clean glass beaker. Analysis of this solution indicate it to be highly pure with respect to transition elements. Data listed in Table 2 show that after two co-precipitation steps all transition element impurities of interest are below the detection limits of the GFAAS. Two additional co-precipitation steps were run in order to verify that the analysis, and purification step were reproducible.

TABLE 2

Purification of Aqueous Lanthanum Nitrate

	Impurity	y concent	tration, ng/g	
<u>Co-Precipitation Step</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>
0*	1158	<7	24	27
1	225	<7	<11	<4
2	<10	<7	<11	<4
3	<10	<7	<11	<4
4	<10	<7	<11	<4
* - i	nitial sample	9		

2. Production of High Purity Lanthanum Carbonate.

Ammonium carbonate, which is purified via co-precipitation, is used to convert the lanthanum nitrate to the carbonate. A 1.6 M solution of ammonium carbonate is prepared by addition of 200g (2.0 mole) of ammonium carbonate to a solution of 1100ml deionized water and 200ml "Ultrex" ammonium hydroxide. The solution is stirred using a mechanical stirrer and 50ml of a 0.1 M barium chloride solution is added slowly. A precipitate of barium carbonate forms immediately and is left to age for 24 hours. The solution is then filtered and the purified ammonium carbonate collected in a clean container where it is diluted to 3.6L making a 0.6M solution. This solution is then halved and saved for later use. The purified lanthanum nitrate solution is

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diluted to 3.1L with deionized water producing an approximately 0.2 M solution. This solution is divided into two equal portions of 1.55L each and both are heated to 90° C on a hot plate. One portion of the hot lanthanum nitrate is then added slowly to 1.8L of the ammonium carbonate solution with stirring, forming a thick white precipitate of lanthanum carbonate.

 $2La(NO_3)_3(aq) + 3(NH_4)_2CO_3(aq) \longrightarrow La_2(CO_3)_3(s) + 3NH_4NO_3(aq)$

The remaining lanthanum nitrate and ammonium carbonate solutions are then mixed forming a second batch of lanthanum carbonate. The precipitated lanthanum carbonate is allowed to settle for 24 hours then filtered on a Buchner funnel using a Teflon membrane filter. After filtration is complete the lanthanum carbonate is washed on the filter with 1L of deionized water. The filter cake is then transferred to a clean container, 1.5 L of deionized water added and the suspension stirred for 1 hour. The washed precipitate is left to age for 24 hours and then filtered through a Buchner funnel using a Teflon membrane filter. The filter cake is then air dried, placed in a clean container and put in an oven at $250^{\circ}C$ for 24 hours to dry. Typically, yields of 180g of lanthanum carbonate (63% yield) are obtained from this process.

TABLE 3

Concentration, ng/g Analysis of Lanthanum and Ammonium Carbonates

<u>Compound</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>
La ₂ (CO ₃) ₃ (NH ₄) ₂ CO ₃ (NH ₄) ₂ CO ₃ CO-DDT	<10 148 2	<10 <2 <2	<10 2 <2	<4 3 <2
LaF3	70	<6	<10	60

Analysis of the ammonium carbonate and the lanthanum carbonate are given in Table 3. The single co-precipitation step for the ammonium carbonate is successful in removing trace amounts of all the transition elements of interest to the low ppb range. This allows for minimal contamination of the lanthanum carbonate due to the ammonium carbonate. The concentration of all transition elements in the lanthanum carbonate are below the detection limits for the GFAAS.

3. Preparation of Lanthanum Fluoride.

A solution of 150ml high purity hydrofluoric acid and 90ml deionized water is prepared (in an acid cleaned teflon container) To this solution 120g of high purity lanthanum carbonate is slowly added with stirring. This reaction is exothermic and accompanied by the evolution of carbon dioxide, therefore care must be taken in this step to avoid spattering and loss of

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product.

 $La_2(CO_3)_{3(s)} + 3HF_{(aq)} \longrightarrow 2LaF_{3(s)} + CO_{2(g)} + H_2O$

After all the lanthanum carbonate has been added the resulting slurry is stirred for 1 hour then left to age for 24 hours at which time it is filtered on a Buchner funnel with a Teflon membrane filter. The filter cake is washed with 1 L of deionized water, air dried, then dried in an oven at 250°C for 24 hours. Typically, yields of 92g of lanthanum fluoride (90% yield) are obtained from this process.

Currently lanthanum fluoride cannot be successfully analyzed using GFAAS due to its low solubility in aqueous acids. However, the use of Spark Source Mass Spectrometry (SSMS) allows for the quantitation, within limits, of the impurities of interest. Analysis by SSMS of the lanthanum fluoride produced from the ultra pure carbonate, listed in Table 3, indicate that contamination of the lanthanum fluoride with iron and copper occurs in the hydrofluorination step. The source of this contamination is presently unknown but reflects our experience in the hydrofluorination of sodium carbonate for the preparation of fluoride. Experiments are currently under way sodium to determine if aging of the precipitated lanthanum fluoride has any effect on the impurity concentration.

<u>Conclusions</u>

High purity lanthanum nitrate and carbonate have been produced containing less than 10 parts-per-billion transition element impurities. Purification was achieved by coprecipitation of lanthanum hydroxide, followed by aging the precipitate for 24 hours. Hydrofluorination of lanthanum carbonate using high purity hydrofluoric acid produced lanthanum fluoride containing measurable traces of iron and copper, while the cobalt and nickel were below detection limits. High quality fluoride glasses (ZBLAN) can routinely be prepared from the lanthanum fluoride produced using this procedure.

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