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CONSERVATION

DIAGNOSIS OF SOURCES OF CURRENT INEFFICIENCY
IN INDUSTRIAL MOLTEN SALT ELECTROLYSIS
CELLS BY RAMAN SPECTROSCOPY

By
Donald R. Sadoway

July 29, 1988

Work Performed Under Contract No. FG07-82CE40545

For
U. S. Department of Energy
Idaho Operations Office
Idaho Falls, Idaho

By
Materials Processing Center
Massachusetts Institute of Technology
Cambridge, Massachusetts

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Introduction

It is somewhat ironic that the least dense structural metals, aluminum and magnesium, which can reduce the nation's net energy consumption when used as materials of vehicular construction, are among the most energy intensive metals to produce. The extraction of light metals is achieved for the most part by molten salt electrolysis, a very energy intensive process. In 1986 the production of primary aluminum and magnesium in the United States consumed 2.3% of total generated electricity in this country.[†] This was not 2.3% of the electricity that went to the metals industry, but 2.3% of *total generated electricity*. The industrial molten salt electrolysis cells that produce these metals operate at power efficiencies of less than 40%. Clearly, there is much to be gained in terms of energy conservation from technological improvements in the extraction of these metals.

From the standpoint of productivity and international competitiveness, reducing the energy consumption of these extraction processes is a high priority. For example, in the United States the average value for the specific energy consumption of aluminum is 7.2 kWh/lb. When power costs were in the vicinity of \$0.005/kWh this amounted to approximately 3.6 cents per pound of aluminum. However, in recent years the cost of electricity has risen to the point where some domestic producers are now paying in excess of \$0.035/kWh. At the same time some foreign producers enjoy access to electricity priced below \$0.010. Thus, the discovery of means to improve the energy efficiency of the smelting process is a way to offset the advantage that derives from low cost power.

[†] This calculation requires a knowledge of metal tonnage [1], generated electricity [1], and specific energy consumption of aluminum [2] and magnesium [3].

The potential for energy savings is substantial. On the basis of 1986 figures (see footnote on page 1 of this report) an improvement of 1% in current efficiency represents an annual energy savings of approximately 5×10^{12} BTU or 5 milliquads.

Reducing energy consumption in industrial molten salt electrolysis operations has been the goal of many research efforts, which for the most part employed *ex situ* methods. Owing to advances in instrumentation there has been a growth in the number of techniques for *in situ* characterization of electrochemical processes. However, in spite of their potential to reveal the nature of electrochemical phenomena, few of these techniques have been used in the study of molten salt electrolysis because, unfortunately, they are not easy to employ in such extreme environments. A case in point is Raman spectroscopy.

Raman spectroscopy is a technique acknowledged to be extremely valuable in the study of ionic species in which complex formation occurs [4]. Industrial molten salt electrolysis is conducted in precisely such chemistries, *i.e.*, electrolytes in which complex ions are present. Indeed, the electrolyte is typically designed so that the ion of the metal being extracted is fully complexed. For example, in the chloride based electrolytes for electrolysis of magnesium and aluminum the ions of these metals are present as tetrachloromagnesate (MgCl_4^{2-}) and tetrachloroaluminate (AlCl_4^-), respectively. In the cryolite based electrolyte used in the Hall-Heroult electrolysis of aluminum its ion is present in a number of fluoroaluminate and oxyfluoroaluminate complexes. While molten salts containing these entities had been studied by Raman spectroscopy, the specific melt compositions were far removed from those employed industrially. Furthermore, there were no reports in the literature of Raman measurements of molten salts during electrolysis. This report summarizes Raman spectroscopy of cryolite based molten electrolytes and includes excerpts from otherwise unpublished project

quarterly reports in the Appendices for completeness. Previous project work is presented in the published report DOE/CE/40545-20.

Objective

Accordingly, the purpose of this project was to employ Raman spectroscopy in the study of industrial molten salt electrolysis cells. The objective was to improve the understanding of the chemistry and electrochemistry of the relevant melt systems and, in turn, of energy loss mechanisms in the industrial processes. On this basis new ways to improve the energy efficiency of these industrial reactors might be identified.

The research plan had several principal elements. First, there was the design and construction of laboratory scale representations of industrial molten salt electrolysis cells that would at the same time serve as spectrocells. Secondly, there was the mastery of the preparation of the molten salt electrolytes, what in industry is called the "front end". Thirdly, there was the adaptation of commercially available Raman instrumentation in order to facilitate the proposed studies. It is the nature of the specimens that so dramatically distinguished this work from conventional Raman studies for which commercial instrumentation is designed: first, the laboratory scale electrolysis cells are large compared to typical spectrocells; and secondly, the cells operate at, what for Raman studies are, extremely high temperatures.

The range of industrial chemistries investigated spanned chlorides and fluorides: magnesium chloride electrolysis (I.G. Farben chemistry), aluminum chloride electrolysis (Alcoa Smelting Process chemistry), and aluminum electrolysis from cryolite (Hall-Heroult chemistry). This also

proved to be the order of investigation of the various chemistries:

Results

The results can be classified according to the specific industrial chemistries cited above. Magnesium chloride electrolysis was studied first for two reasons. First, laboratory scale electrolysis cells could be constructed of fused quartz; secondly, there were reports in the literature of Raman measurements of molten $MgCl_2$ and solutions of $MgCl_2$ with various alkali chlorides. Aluminum chloride electrolysis was studied next. The results of both the magnesium chloride work and the aluminum chloride work were described previously in the publicly available topical report, DOE/CE/40545-20 which summarizes the activities of the project from its inception in May 1982 through June 1987.

Hall cell chemistry was the third principal focus of this project. The results of the Raman study of Hall cell chemistry are presented with reference to the "Cryolite Test Plan", a document filed with the contracting officer in September 1987 and reproduced in Appendix A.

Part 1: The chemistry of cryolite-based melts

At the time the Cryolite Test Plan was filed it had already been recognized that melt contamination by the container was a potential problem. On the basis of laboratory experiments it had been shown that fused quartz was totally unacceptable and there were doubts as to the degree of inertness exhibited by sapphire.

Fused quartz was unable to contain molten cryolite under the specific furnace conditions of this investigation. The heat transfer

rates to the solid salt were such that by the time the entire sample had become molten the walls of the cell had been severely attacked. The result was that in some cases the melt broke through the cell wall before data could be taken; in other cases when there was enough time to take data the melt composition had changed so much that the data were meaningless. Certainly the use of fused quartz is to be avoided when one wishes to control the oxygen level of a fluoride melt.

The earliest successful results for cryolite were obtained in spectrocells made of single crystal sapphire tubing. The spectra appear in an article published in Light Metals 1986 and in a quarterly project report, DOE/CE/40545-11 (Appendix B). Attempts to reproduce these results and improve signal to noise ratio were frustrated. One of the problems was the apparent shift to higher wave numbers in the position of the dominant peak. In the early studies this peak was found to be near 535 cm^{-1} : 535 cm^{-1} reported in DOE/CE/40545-11 and 533 cm^{-1} reported in DOE/CE/40545-15 (Appendix C). However, in later studies this same peak was observed at values in the vicinity of 560 cm^{-1} . It became evident after many carefully controlled experiments that this variation was caused by the presence of dissolved oxide. Apparently, even though sapphire was much more resistant to attack by the melt than was fused quartz, there was still enough oxide present even at short times, presumably in the boundary layer at the cell wall, to cause the observed shift in wave number.

The response was to design and construct a spectrocell of material totally resistant to attack by cryolite, or at least a material with corrosion products that are not Raman active and do not alter the spectrum of pure cryolite. The Cryolite Test Plan indicated that one approach was to employ an inert crucible of graphite or boron nitride and to suspend the melt from an inert metal wire helix held above the crucible, the entire crucible and wire assembly contained inside an

outer fused quartz tube to maintain an inert gas atmosphere. This was attempted with a number of configurations using gold wire, platinum wire, and titanium diboride both in sheet form with a hole drilled through and in rod form for pendant drop studies. The physical chemistry of the system simply was not favorable. The relative surface energies combined the fluidity of molten cryolite caused this design to fail.

The first spectra of oxide free cryolite were obtained using the spectrocell described in the project quarterly report DOE/CE/40545-23 (Appendix D). This was the cell in which melt was forced by piston up into a groove cut part way across the sidewall of a cylindrical crucible. The crucible and plunger were composed of inert material such as boron nitride. Under these conditions the dominant peak was located at $\approx 580 \text{ cm}^{-1}$ as reported in the project quarterly report DOE/CE/40545-24 (Appendix E).

To obtain oxide free cryolite, contain it, and take its Raman spectrum was an extremely difficult problem. However, the effort to solve this problem led to two important discoveries:

1. *there is a relationship between the position of the dominant peak and the Al_2O_3 content of the melt.*
2. *the ratio of cryolite to AlF_3 is expressed in the Raman spectrum.*

These relate directly to Tasks 1.3 and 1.2, respectively, of the Cryolite Test Plan. The results have been fully described in the above referenced quarterly report. The significance of this work is that *the concept of compositional measurement in cryolitic melts by Raman spectroscopy has been demonstrated.*

The measurement of cryolitic melts containing CaF_2 (Task 1.4 of

the Cryolite Test Plan) was attempted without success. Several experiments were conducted. In all cases the spectra appeared identical to those of pure cryolite. This may suggest that calcium is present as a discrete ion, i.e., not part of a complex, and thus is not detectable by Raman spectroscopy.

Careful measurement of the spectra of cryolite in boron nitride and graphite showed no difference (Task 1.5 of the Cryolite Test Plan).

Attempts to measure the spectra of melts to which elemental metal had been added failed. Tasks 1.6 and 1.7 of the Cryolite Test Plan were to look at the effects of additions of aluminum and sodium, respectively. The problem was materials of construction for the spectrocell. Aluminum attacks boron nitride and reacts with graphite. Attempts to use the sapphire cell were foiled. The addition of metal caused the melt to darken and an opaque film to form on the wall of the cell thereby obstructing the beam.

Part 2: Conventional Hall cell electrolysis

Attempts to measure changes caused by the passage of current were unsuccessful. Once electrolysis began, a variety of insurmountable problems presented themselves. First, the signal to noise ratio became unacceptably poor. This meant that it became impossible to appreciate any changes in the spectrum that might occur as a result of the presence of new chemical species. Furthermore, in some cases the electrolyte darkened and an opaque film formed on the inner wall of the cell. The latter was usually a sign of aluminum solubility. All of this was disappointing, as a rather ingenious design of a miniature Hall cell had been developed after considerable effort. Attempts to render the piston spectrocell into an electrolysis cell were unsuccessful. Perhaps there still is some way to take Raman data during electrolysis in a

laboratory scale, but this remains to be discovered. At this point an approach involving fiber optics is recommended.

Part 3: Effects of impurities on melt chemistry

Owing to experimental difficulties, execution of Parts 1 and 2 of the Cryolite Test Plan took more time than originally anticipated with the result that Part 3 received less attention. The only impurity investigated was silicon, which was added to pure cryolite as SiO_2 . At levels representative of those encountered in Hall cell bath the Raman spectrum appeared identical to that of pure cryolite. At very high levels typical of those found when cryolite attacks fused quartz, the spectrum of cryolite was observed to deteriorate; while no new peaks were observed, for the peaks in the spectrum of pure cryolite itself there was a general broadening along with a decrease in peak-to-background ratio.

Part 4: Hall cell electrolysis with conventional bath containing impurities

See remarks above in Part 2.

Part 5: Effects of unconventional additives on melt chemistry

Attempts were made to measure the effects of the addition of Li_3AlF_6 on cell bath. Results were disappointing as no change was observed in the spectrum of pure cryolite. However, it should be noted that these experiments were performed early in the investigation. Perhaps if the experiments were repeated with the more advanced spectrocells the presence of Li_3AlF_6 might be detectable. Certainly on the basis of the work performed during the course of this investigation it would be inappropriate to dismiss Raman spectroscopy as a useful

technique in this regard. More study is necessary before a decision can be made one way or the other.

Part 6: Hall cell electrolysis with conventional bath containing unconventional additives: "unconventional bath"

See remarks above in Part 2.

Other studies

As part of a study of bath chemistries that would support a nonconsumable anode the Raman spectrum of ZrO_2 dissolved in cryolite was measured. Figure 1 shows the results. The bath consisted of 15 wt% ZrO_2 as weighed against cryolite before melting. The temperature of the measurement was $1020^\circ C$ and the excitation radiation had a wavelength of 488 nm. At first glance the spectrum appears identical to that of pure cryolite. However, the main peak is found at a value of wave number shift lower than that of pure cryolite and higher than that of cryolite saturated with alumina. While these results are preliminary they take on significance when viewed in the context of the conclusions cited above about the relationship between alumina concentration and wave number shift of the major peak. While further study is necessary to explain the observation in Figure 1, this still could be a demonstration of the ability of the Raman technique to measure the oxygen potential of the bath as well as metal oxide solubility in general.

In this regard Figure 2 is presented. It shows much the same data as reported in Appendix E, but this time with the aid of the phase diagram on the same page. Clearly, the solubility limit is identifiable in the concentration dependence of the wave number shift. The Raman data give a value of 13 wt% at a temperature of $1030^\circ C$. This compares favorably with the value of 14 wt% shown in the phase diagram. In

principle, the same approach could be taken to determine bath compositions and solubility limits in a wide variety of industrially important molten salts. It should be remembered that with the piston spectrocell these measurements are relatively simple to make.

Summary

This project began as an attempt to investigate the applicability of Raman spectroscopy to the study of the chemistry and electrochemistry of industrial molten salt electrolysis with the intention of diagnosing sources of loss of current efficiency. The success of this work should then to a large extent be assessed in the light of this objective. What, then, are the accomplishments? The answer to this question has many parts broadly falling into several categories: scientific, technological, and educational.

First, the scientific accomplishments. This was the first study of its kind that sought to use Raman spectroscopy as an investigative tool in the study of the chemistry and electrochemistry of industrial molten salt electrolysis. As such, there were many accomplishments at the laboratory scale that will serve as the basis for future studies. Among these were the development of laboratory scale representations of industrial molten salt electrolysis cells that simultaneously served as spectrocells; so-called spectroelectrochemical cells. Given the severe chemistries that one encounters in such systems this was not trivial. In 1982, when this investigation began, this kind of hardware was unknown. Today, spectrocells of the type developed in this investigation as well as the furnaces to go with them are showing up in laboratories all over the world. For chlorides, there is the use of fused quartz tubing of square cross section. For fluorides, there is the use of the sapphire single crystal-tubing and the piston spectrocell. These are all products of this investigation and represent

advances for the field.

Secondly, there are laboratory techniques that have been introduced into the field as a result of this investigation. Most notably, there is the use of thionyl chloride, SOCl_2 , in the *in situ* purification of magnesium chloride melts and aluminum chloride melts.

Now, the technological accomplishments. During the course of this study it became apparent that Raman spectroscopy has the capability to analyze melt composition. In the system, AlCl_3 - KCl (see topical report DOE/CE/40545-20), this was shown vividly as the Al content was measured from 25 mole % AlCl_3 down to 1 mole % AlCl_3 . The salient features of this were that the dependence of intensity on concentration of AlCl_3 was linear and the calibration curve went through the origin on a plot of intensity versus mole per cent AlCl_3 . Analogous measurements could be made to determine the concentration of MgCl_2 in alkali and alkaline earth halide solvent melts. As molten chlorides do not attack fused quartz readily, the use of fiber optics in order to measure such spectra with a view to determining the melt composition is not out of the realm of possibility and with little effort could be implemented with technology available today.

In the case of fluoride melts, the electroactive species may be involved in other bonding besides metal-fluorine complexing. Some of these bonds involved oxygen. The metal-oxygen bond is Raman active. The ability to detect this bond gives one the ability to analyze for oxygen in such melts, a very important control parameter. Again as in the case of the chlorides cited above, one can imagine a system involving fiber optic probes, but in the special case of fluorides these probes would have to be encased in some kind of refractory insulation. In operation the probe tip would be consumable but have a service life longer than the time required to take a measurement. Knowledge of the

precise oxygen content of the bath would be very useful in a control strategy. For example, this would enhance alumina feeding and allow cells to operate nearer optimum concentration, thereby improving their power efficiency as well as their productivity or space-time yield.

The important point worth making about Raman spectroscopic analysis of melts is that the use of fiber optic probes renders the technique immune to electromagnetic interference, an extremely important attribute for a technique to be used in industrial molten salt electrolysis cells where the high electrical currents, typically 100 to 300 kA, give rise to intense magnetic fields. To take meaningful electrical measurements under such conditions requires the use of elaborate shielding and extensive signal processing. Spectroscopic techniques require none of the former and less of the latter.

Finally, the educational accomplishments. The continued sponsorship of this research at MIT over the past 6 years has done much to enhance the infrastructure of molten salt research in this country. Molten salt electrochemistry, and in particular, materials processing by molten salt electrochemistry, is a field of study that has been largely ignored here in the U.S. This in contrast to the sustained efforts in Western Europe and the Soviet Union as well as the strong emerging effort in Japan.

This research project was in many respects the focal point of what was to become for the principal investigator a portfolio of projects in the field of molten salt electrochemistry to serve as the basis for a molten salt group at MIT. The unique perspective that this molten salt group brings to the field is its emphasis on fundamentals while addressing issues of industrial interest. Furthermore, what makes the study of molten salt electrochemistry in the context of materials processing unique is that the students are made well aware of the

interrelationships between processing, structure (microstructure and composition), and properties. In this sense, the students who come in contact with this research effort, either by direct participation through thesis research or indirectly through courses taught by the principal investigator, are exposed to a different set of issues from those encountered in departments of Chemistry or Chemical Engineering.

Finally, the presence of a research effort of this kind has attracted many industrial scientists back to the university campus, as evidenced by the number of such visits documented in the reports filed during the course of this investigation. At a time when policy makers are expressing concern over technology transfer and its effects on international competitiveness the stimulation of such university-industry interactions should be recognized and applauded.

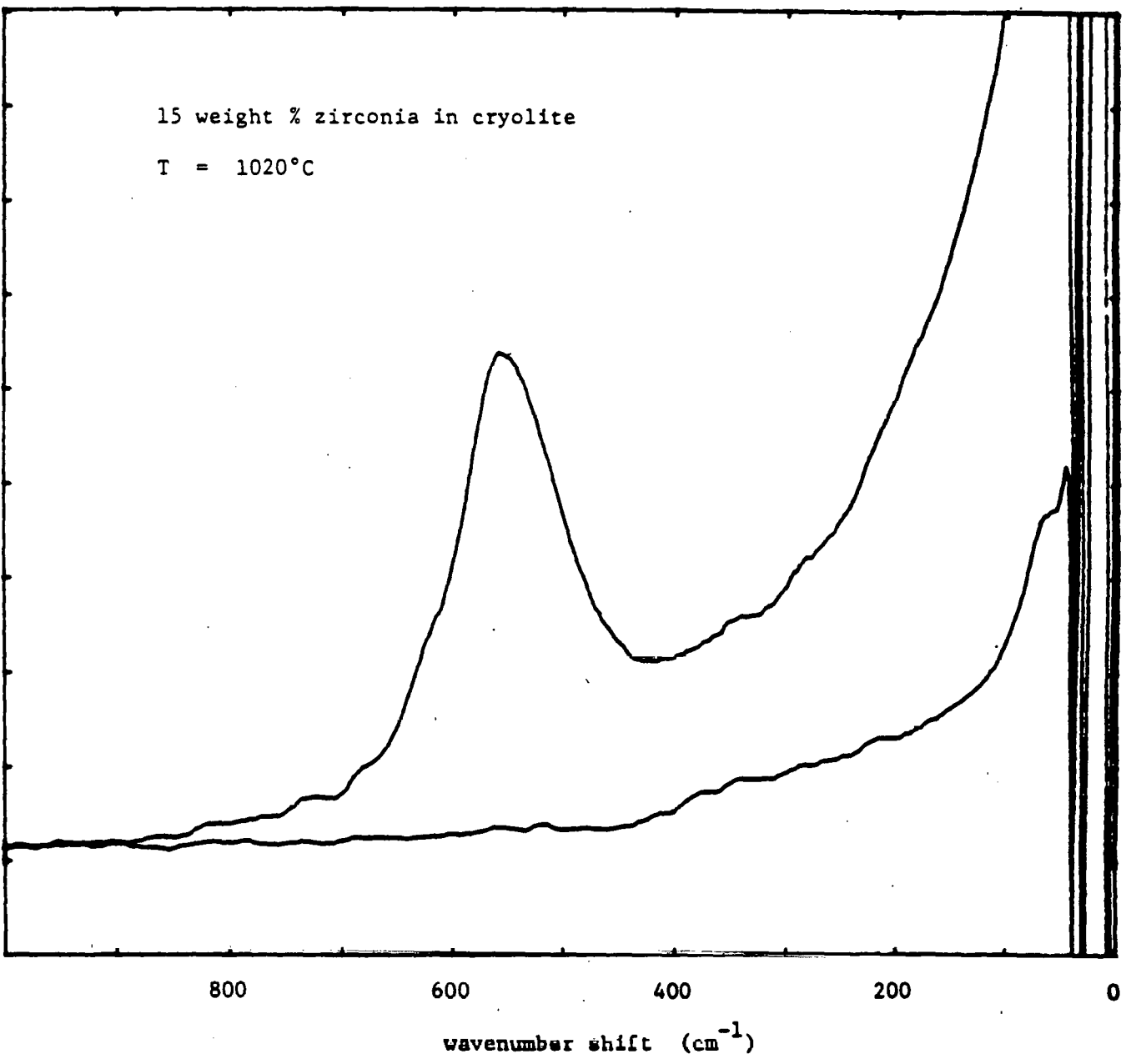
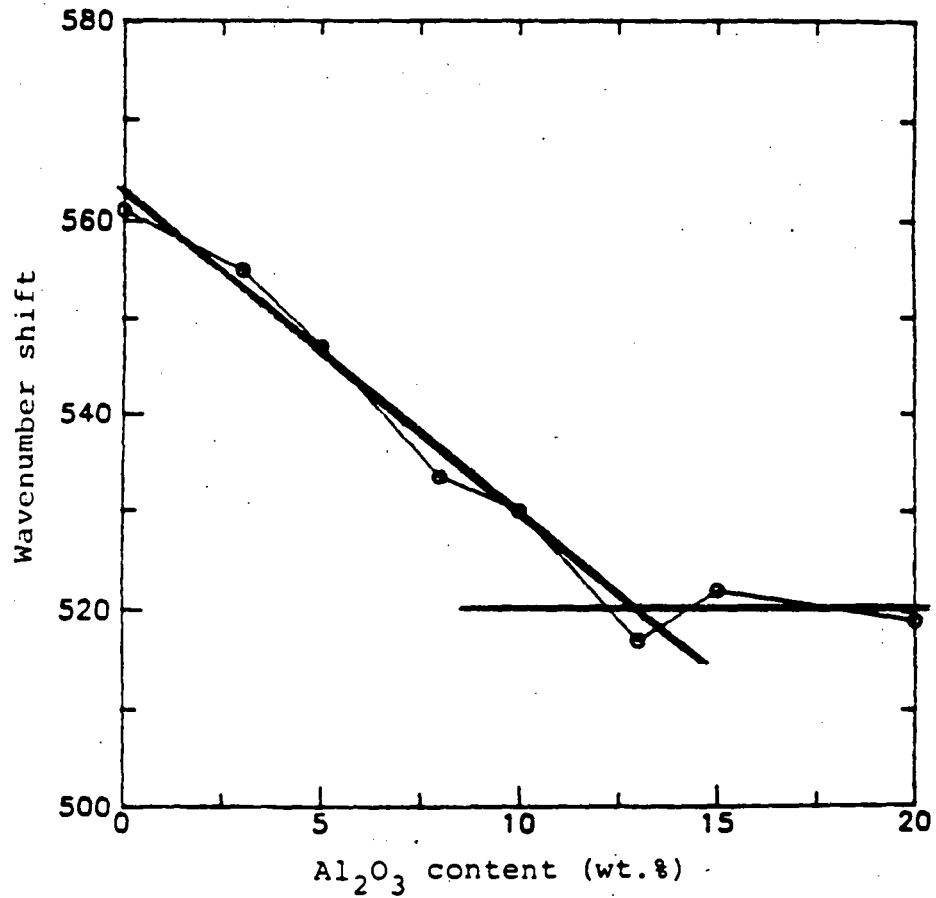
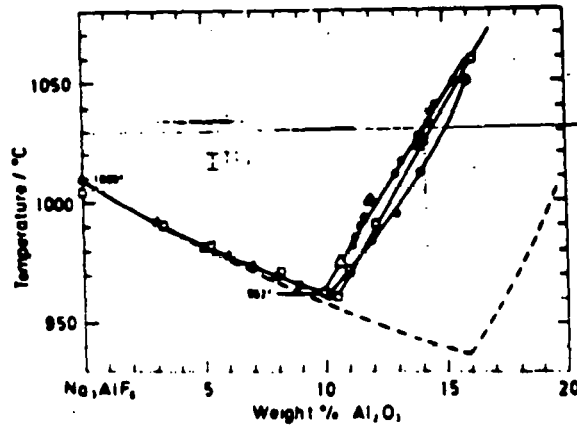


Figure 1. Raman spectrum of zirconia in cryolite.

Figure 2. Raman spectrum of alumina dissolved in cryolite.



Dependence of wavenumber shift on alumina content in cryolite



List of Publications

1. S.-Y. Yoon, J.H. Flint, G.J. Kipouros, and D.R. Sadoway, "Raman Scattering Studies of Molten Salt Electrolysis of Light Metals," Energy Reduction Techniques in Metal Electrochemical Processes, R.G. Bautista and R. Wesely, editors, TMS-AIME, Warrendale PA, 1985, pp. 479-490.
2. G.J. Kipouros, J.H. Flint, and D.R. Sadoway, "Raman Spectroscopic Investigation of Alkali-Metal Hexachloro Compounds of Refractory Metals," Inorg. Chem., 24, 3881, 1985.
3. S.-Y. Yoon, Y. Liu, J.H. Flint, G.J. Kipouros, and D.R. Sadoway, "In Situ Raman Spectroscopic Investigation of Melt Chemistry and Electrode Processes in Laboratory-scale Aluminum Cells," in Light Metals 1986, R.E. Miller, editor, TMS-AIME, Warrendale PA, 1986, pp. 479-482.
4. S.-Y. Yoon, J.H. Flint, G.J. Kipouros, and D.R. Sadoway, "Raman Scattering Studies of Magnesium Electrolysis," in Light Metals 1986, R.E. Miller, editor, TMS-AIME, Warrendale PA, 1986, pp. 1009-1012.
5. S.-Y. Yoon and D.R. Sadoway, "Spectroelectrochemical Study of Magnesium Electrolysis," in Light Metals 1987, R.D. Zabreznik, editor, TMS-AIME, Warrendale PA, 1987, pp. 851-859.
6. G.J. Kipouros and D.R. Sadoway, "The Chemistry and Electrochemistry of Magnesium Production," in Advances in Molten Salt Chemistry, Vol. 6, G. Mamantov, C.B. Mamantov and J. Braunstein, editors, Elsevier, Amsterdam, 1987, pp. 127-209.
7. D.R. Sadoway, "Raman Spectroscopic Studies of Fused Salt Electrolysis," in Proc. 31st Internat. Cong. Pure and Appl. Chem., Sofia, Bulgaria, Section 7, Phys. Chem., pp. 172-179.
8. S.-Y. Yoon and D.R. Sadoway, "Spectroscopic and Electrochemical Studies of Molten Salt Electrolysis of Aluminum and Magnesium," in Proceedings of the Joint International Symposium on Molten Salts, G. Mamantov et al., editors, The Electrochemical Society, Pennington NJ, 1987, pp. 1011-1017.

In addition to the above cited publications it is expected that there will be three publications based on the doctoral thesis of S.-Y. Yoon.

Acknowledgements

Many people contributed to this research. Their efforts are gratefully acknowledged:

Dr. Seok-Yeol Yoon, who conducted most of the experiments and took almost all the reported data, designed and constructed all the high temperature spectrocells beyond the first generation including the unique "slotted cell" capable of both containment and "windowless" display of the highly corrosive fluoride melts, and recognized ways to treat Raman data so as to be able to use the Raman spectroscopy for quantitative analysis of molten salt solutions;

Dr. Georges J. Kipouros, who established the facilities for purification of salts, built the first high temperature spectroelectrochemical cells, conducted the first experiments to obtain Raman spectra of "near industrial" melts, and during the early stages of this project provided much of the laboratory expertise associated with molten salt chemistry in general;

Mr. John H. Flint, who assembled the system for Raman scattering studies of molten salts, and helped conduct the first experiments and interpret the data;

Ms. Yachin Liu, who helped with some of the first Raman measurements of cryolite melts.

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1. B.V. Tilak and J.W. Van Zee, "Report of the Electrolytic Industries for the Year 1986," *J. Electrochem. Soc.*, 134, 297C-316C (1987).
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APPENDIX A
CRYOLITE TEST PLAN

CRYOLITE TEST PLAN

The following test plan outlines the experiments to be performed under Tasks 6, 7, and 8 of Grant No. DE-FG07-82CE40545, Mod. 004. The purpose of the work is to use Raman spectroscopy to determine causes of the loss of current efficiency in Hall cells.

The study plans to look at conventional electrolysis, impurity effects, and unconventional bath additives. At each stage, first the Raman spectra of various melts are taken in the absence of electrolysis.

Part 1 The Chemistry of Cryolite-based Melts

Raman spectra will be measured in the absence of electrolysis. For many experiments a monocrystalline sapphire cell will be used. Tests will also be conducted with the melt contained in crucibles of graphite and boron nitride. In such cases the melt will be suspended from a metal wire helix held above the crucible.

Compositions include the following:

1. Pure cryolite
2. Cryolite + aluminum fluoride at various concentrations
3. Cryolite + alumina at various concentrations
4. Cryolite + calcium fluoride
5. Cryolite in the presence of graphite
6. Cryolite in the presence of aluminum metal
7. Cryolite in the presence of sodium metal
8. Cryolite + aluminum fluoride + alumina + calcium fluoride
9. Composition 8 in the presence of aluminum metal
10. Composition 8 in the presence of sodium metal

The results of Items 2 and 3 will attempt to determine whether Raman spectroscopy can determine bath ratio and alumina concentration, respectively.

Part 2 Conventional Hall Cell Electrolysis

In these experiments, a purified conventional bath is used. Electrolysis will be conducted in a monocrystalline sapphire cell with a graphite anode and graphite cathode block covered with a pool of molten aluminum. Bath consists of cryolite, alumina, and aluminum fluoride such that bath ratio is near 1.15. The presence of CaF_2 will be optional. Current density will be varied from 10 mA/cm^2 to 1 A/cm^2 .

Part 3 Effects of Impurities on Melt Chemistry

Raman spectra will be measured in the absence of electrolysis. For many experiments a monocrystalline sapphire cell will be used. Tests will also be conducted with the melt contained in crucibles of graphite and boron nitride. In such cases the melt will be suspended from a metal wire helix held above the crucible.

Compositions include the following:

1. Cryolite + impurity
2. Cryolite + impurity + alumina
3. Cryolite + impurity + graphite
4. Cryolite + impurity + aluminum
5. Cryolite + impurity + aluminum + graphite
6. Cryolite + impurity + alumina + aluminum + graphite

The impurities to be studied are phosphorus, added as P_2O_5 , iron, added as Fe_2O_3 , vanadium, added as V_2O_5 , and silicon, added as SiO_2 .

Part 4 Hall Cell Electrolysis with Conventional Bath Containing Impurities

Repeat experiments of Part 2 but with impurities of Part 3 present in cell bath.

Part 5 Effects of Unconventional Additives on Melt Chemistry

Repeat experiments of Part 3 substituting additive for impurity. The unconventional additive to be studied will be Li_3AlF_6 .

Part 6 Hall Cell Electrolysis with Conventional Bath Containing
Unconventional Additives: "Unconventional Bath"

Repeat experiments of Part 2 but with additives of Part 5 present in cell bath.

APPENDIX B
EXCERPT FROM QUARTERLY PROJECT REPORT
DOE/CE/40545-11

RAMAN SCATTERING STUDIES OF MAGNESIUM ELECTROLYSIS

S.-Y. Yoon, J. H. Flint, G. J. Kipouros*, and D. R. Sadoway
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As part of a study of the causes of the loss of current efficiency in industrial magnesium cells, the characteristics of laboratory-scale cells are being investigated by electrochemical and spectroscopic techniques. Specifically, to determine the factors that control the concentrations and spatial distributions of the various chemical species in the cell, Raman spectra are taken *in situ* during electrolysis. The electrolyte consists of 11% MgCl₂, 65% NaCl, 18% KCl, and 6% CaCl₂. Cells operate at a temperature of 750°C and current densities up to 2 A/cm². Spectral information from all identifiable species is correlated with cell operating conditions in an attempt to understand the nature of such phenomena as metal fog, streamers, and melt coloration, all of which are observed in these laboratory-scale cells.

Introduction

The extraction of light metals is achieved for the most part by molten salt electrolysis, a very energy-intensive process. The production of primary aluminum and magnesium is estimated to have consumed 2.8% of total generated electric power in the United States during the Year 1984[1]. It is somewhat ironic that the least dense structural metals, which can reduce net energy consumption when used as materials of vehicular construction, are among the most energy-intensive metals to produce. Thus, research efforts are directed at reducing the energy requirements of these extraction processes.

The electrolytic production of magnesium accounts for about 70% of the total magnesium production in the Western world[2]. Magnesium production by electrolysis requires 15 - 18 kWh/kg of magnesium metal. The current efficiency of the anhydrous electrolytic process (I.G. Farben - Norsk Hydro) exceeds 90%, while that of hydrous electrolytic process (Dow Chemical) is close to 80%[3].

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As part of a study of the causes of loss of current efficiency, Raman spectra of laboratory-scale magnesium chloride electrolysis cells are being measured. Commercially available laser Raman scattering instrumentation has been adapted to permit *in situ* real-time investigation of melt chemistry and to provide the basis for "fast Raman" spectroelectrochemistry in this and other melt systems. The results of the Raman work are combined with those of other techniques in order to reveal the mechanisms and kinetic pathways that decrease current efficiency in magnesium cells. This paper reports some preliminary Raman data for the electrolysis of anhydrous magnesium chloride.

Literature

Reasons for the loss of current efficiency are discussed in a recent review of the chemistry and electrochemistry of magnesium production[4]. More information is given in the monograph by Strelets[5]. Of particular concern to the Raman work is information on melt structure: magnesium does not exist as a discrete cation in chloride melts but instead in the form of the chlorocomplex, MgCl₂⁻[6-8]. Vibrational spectra confirm this[9-13]. However, the purpose of these studies was to determine the structure of molten salts, not to understand the electrolytic production of magnesium. As a consequence, melt spectra were not taken during electrolysis, nor were they taken of melts resembling industrial compositions.

Experimental

A detailed description of the instrumentation is given in previous reports[14,15]. Very briefly, a monochromatic linearly polarized laser beam from either an Ar⁺ laser (Coherent Innova 90-4) or Kr⁺ laser (Coherent Innova 90-K) irradiates the electrolysis cell which is held inside a specially designed furnace. The scattered light is focused onto the entrance slit of the spectrometer (Spex Industries Triplemate 1403). An intensified silicon photodiode array (EG&G PARC Model 1420-3) serves as detector. The amplified signal is digitized in the detector

controller (EG&G PARC Model 1218) and transmitted as data to the optical multichannel analyzer (EG&G PARC, OMA, Model 1215).

The polarization state of the exciting radiation is set by a polarization rotator ($\perp I_1$ or $\parallel I_1$). The beam then passes horizontally through the electrolysis cell. The scattered radiation is collected at 90° and is imaged onto the vertical polarization analyzer (I_2 always). The spectrometer slit width is $100 \mu\text{m}$, equivalent to $\sim 6 \text{ cm}^{-1}$. Typically, the spectra were recorded for approximately 1 minute, corresponding to 200 scans on the OMA, which was calibrated using the emission lines of a neon lamp in the green. All spectra reported in this article were obtained using the 514.5 nm line of argon as exciting radiation.

The electrolysis cell is constructed of optical-grade square fused quartz tubing, 1" on inside edge, joined to round tubing 41 mm O.D. The cap is a compression fitting made of 304 stainless steel and has ports for the cathode, anode, inert gas inlet, and thermocouple. The cap also has a sidearm for gas outlet.

The anode is made of high-density graphite rod, 1/8" dia., usually shrouded by a fused quartz tube, 3/8" dia. For the cathode, mild steel, 1/4" dia., TiB_2 single crystal, 1 mm dia., or high-density² graphite rod, 1/8" dia., shrouded by an alumina tube, 3/8" dia., have all been used.

The preparation of anhydrous salts for electrolyte formulation has been described previously[14].

In a typical experiment, the electrolysis cell is charged with salt and assembled with the cap and electrodes in the glove box. The charged cell is placed in the electrical resistance furnace with windows[14], and the salt is melted under high purity argon.

Results and Discussion

Figure 1 shows Raman spectra of pure molten MgCl_2 at 740°C . There is a strong polarized peak at 205 cm^{-1} and a weak depolarized peak at 385 cm^{-1} . These results are essentially identical to those of Huang and Brooker[10]. The difference is that it took the authors of this report only 4 minutes using the OMA to measure these spectra which Huang and Brooker recorded for several hours. This shows the speed, accuracy, and sensitivity of the adapted instrumentation to be satisfactory.

Figure 2 shows Raman spectra of the melt, 78% NaCl and 22% KCl, at a temperature of 840°C . There are no "peaks" like those seen in Figure 1. However, the featureless traces in Figure 2 derive from inelastic scattering and are proper Raman spectra.

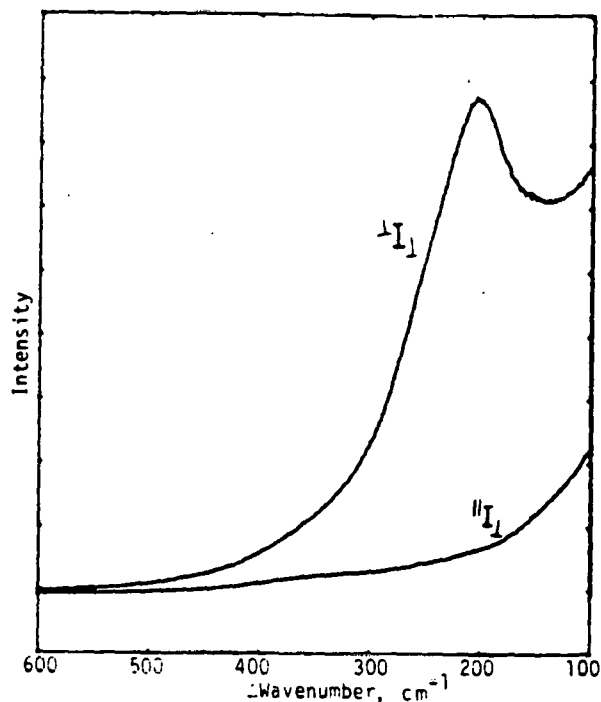


Fig.1 Raman spectra of molten magnesium chloride at 740°C .

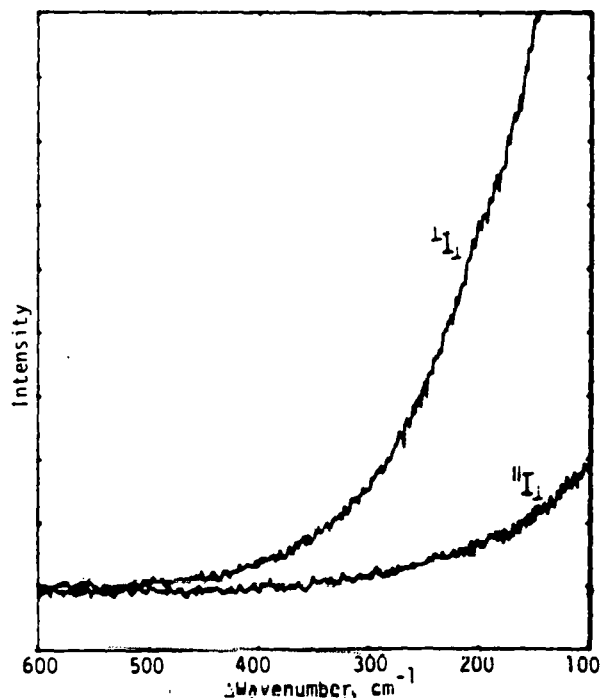


Fig.2 Raman spectra of molten 78w/o NaCl - 22w/o KCl at 840°C .

Figure 3 shows Raman spectra of the supporting electrolyte, 7% CaCl_2 , 20% KCl , and 73% NaCl , taken at a temperature of 850°C . Somewhat surprisingly, the addition of CaCl_2 to the alkali chloride melt did not give rise to any distinct peaks. It was hoped that one or more such peaks could be used as a standard for calibrating composition during electrolysis experiments. The CaCl_2 content is not expected to change while magnesium is produced.

Figure 4 shows Raman spectra of a melt representative of industrial composition (11% MgCl_2 , 6% CaCl_2 , 65% NaCl , 18% KCl) taken at a temperature of 750°C in the absence of current. The prominent polarized peak at 205 cm^{-1} in pure MgCl_2 has shifted to 249 cm^{-1} . During electrolysis there was a decrease in peak height without change in wavenumber for the peak at 249 cm^{-1} .

Figure 5(a) shows a photograph of the cell taken after 1 minute of electrolysis at a current density of 100 mA/cm^2 . The composition of the electrolyte was 11% MgCl_2 , 65% NaCl , 6% CaCl_2 , and 18% KCl . Temperature was 750°C . On the left is a $1/4$ " graphite cathode; on the right is a $1/8$ " graphite anode shrouded with fused quartz tubing. Streamers have begun to emanate from the cathode. Chlorine gas bubbles can be seen on the anode. Figure 5(b) shows the same cell as Figure 5(a) after approximately 5 minutes of electrolysis at a current density of 100 mA/cm^2 . It is evident that the streamers emanating from the cathode have grown over essentially the entire breadth of the cell. The electrolyte has become cloudy. Figure

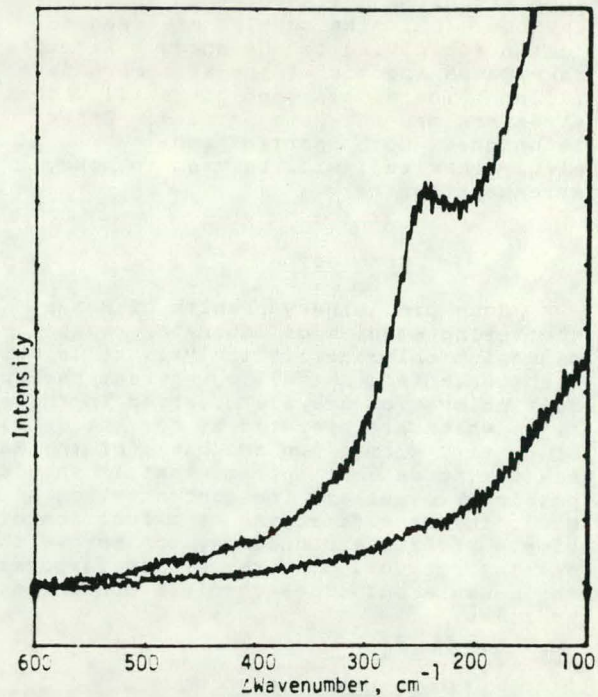


Fig. 4 Raman spectra of molten 11w/o MgCl_2 - 6w/o CaCl_2 - 65w/o NaCl - 18w/o KCl at 750°C .

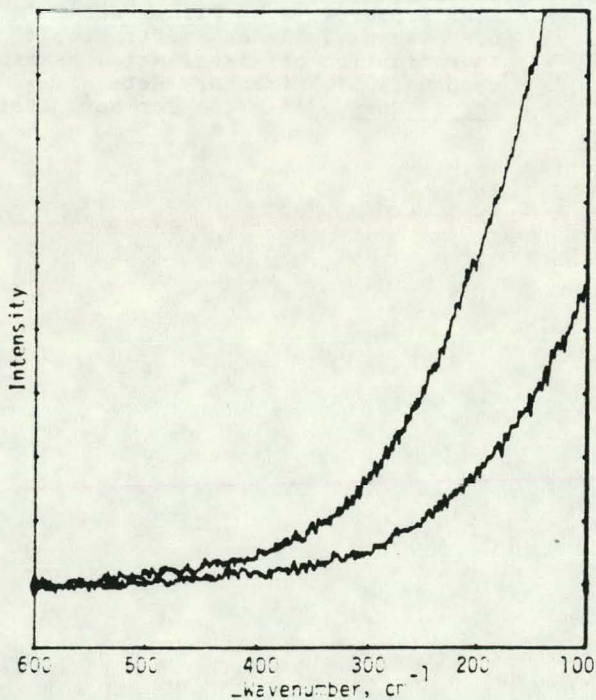


Fig. 3 Raman spectra of molten 7w/o CaCl_2 - 20w/o KCl - 73 w/o NaCl at 850°C .

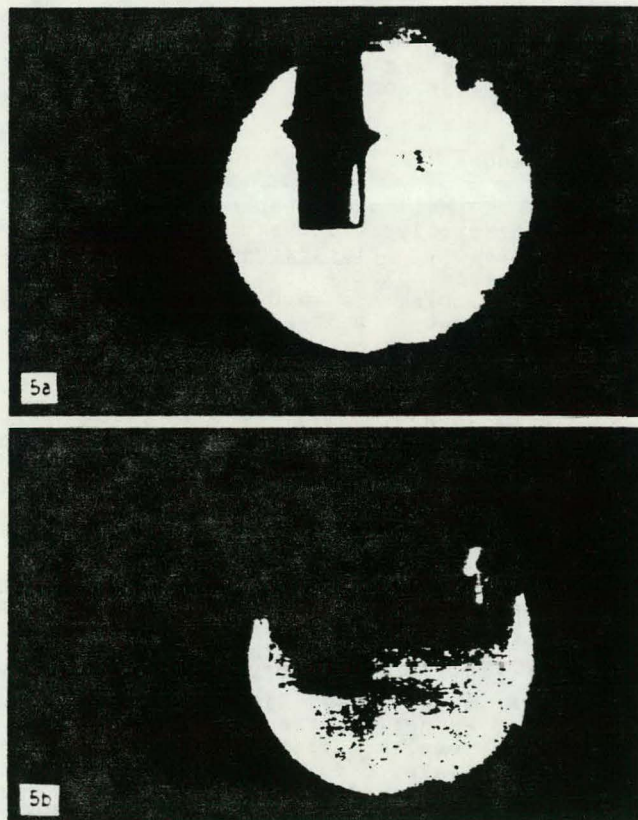


Fig. 5 Streamer development in a laboratory-scale magnesium electrolysis cell. Electrolyte: 11w/o MgCl_2 - 6w/o CaCl_2 - 65w/o NaCl - 18w/o KCl . $T = 750^\circ\text{C}$. Current density = 100 mA/cm^2 . (a) after 1 minute; (b) after 5 minutes.

5(b) also shows the appearance of tiny droplets of magnesium on the tip of the cathode. Chlorine bubbles are seen to continue evolving on the anode. Attempts to take Raman spectra of the streamers have failed. There is a good possibility that the streamers are not Raman active. Other techniques, both spectral and electrochemical, will be used to study streamers further.

Conclusion

Some preliminary results of Raman scattering studies of laboratory-scale magnesium chloride electrolysis cells have been presented. Metal fog, streamers, and melt coloration are all observed in these cells which are operated at current densities of up to 2 A/cm². On the basis of the Raman scattering data it appears that it should be possible to measure the concentration of MgCl₂ in the electrolyte as a function of time. Efforts are underway to improve the spatial resolution of the system to permit the measurement of electrolyte concentration profiles.

Acknowledgement

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APPENDIX C

EXCERPT FROM QUARTERLY PROJECT REPORT

DOE/CE/40545-15

EXCERPT FROM QUARTERLY PROJECT REPORT
DOE/CE/40545-15

Following is the Raman spectroscopy technical discussion relevant to cryolite based electrolytes:

Cryolite

The single crystal sapphire tube, closed at one end, was tested in a spectrocell with molten cryolite. It proved to be able to survive the thermal cycle of heating to 1015°C, containing molten cryolite, and cooling to room temperature with the solidification of molten cryolites. When the solidified cryolite was dissolved in an aqueous solution of aluminum chloride, the sapphire showed no evidence of etching or loss of transparency.

Cryolite spectra were taken in the sapphire spectrocell. Three stokes (red Raman) shifts were observed: 180, 390, and 533 cm^{-1} . The 533 cm^{-1} line is strongest and polarized, while the one at 390 cm^{-1} is weak and depolarized. The 180 cm^{-1} line is in the anomalous Rayleigh shoulder and is depolarized. The spectrometer was also scanned to deeper red to search for higher wave number Raman shifts. None were detected.

Electrolysis was attempted in a single crystal sapphire tube, open at both ends. The bottom of the tube was plugged with graphite, which also served as the cathode. Unfortunately the seal was poor, and the electrolyte leaked out upon melting. The cell has been redesigned to incorporate a longer cathode plug so that the freeze line forms midway along the plug, i.e., between the bottom of the melt and the bottom of the open-ended sapphire tube.

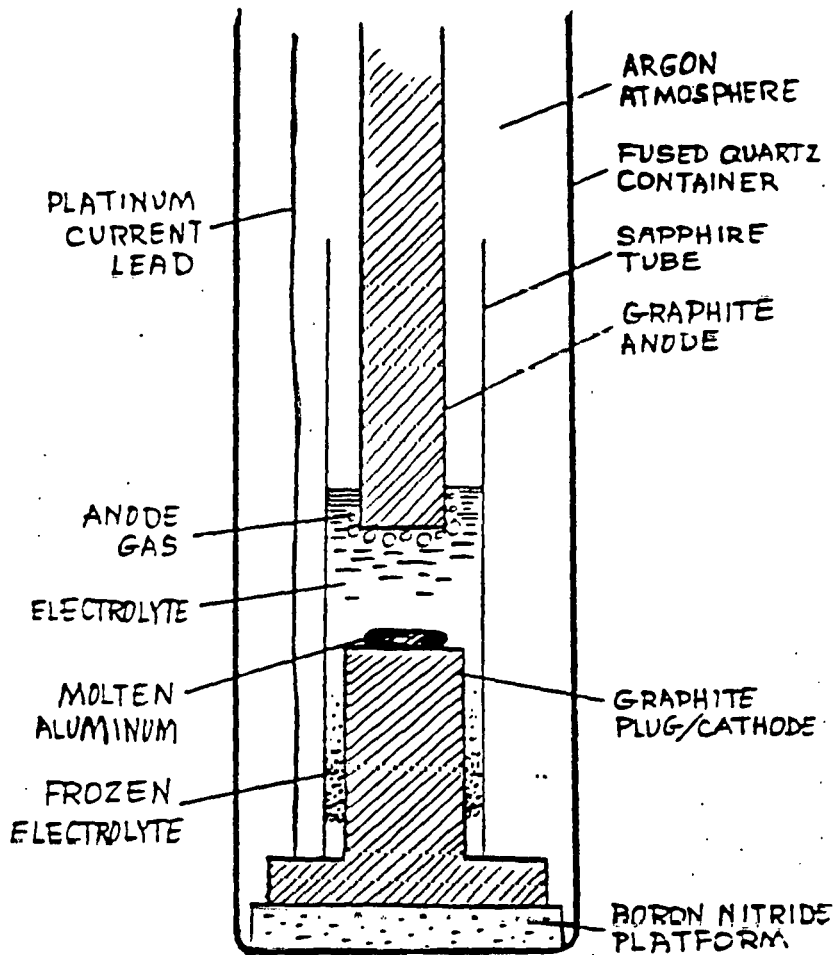


Figure 1 Schematic of Laboratory Scale Hall Cell
 for simultaneous Raman and Electrochemical
 Studies.

APPENDIX D

EXCERPT FROM QUARTERLY PROJECT REPORT

DOE/CE/40545-23

EXCERPT FROM QUARTERLY PROJECT REPORT
DOE/CE/40545-23

Following is a discussion of research accomplishments from the quarterly project report DOE/CE/40545-23:

This quarter was marked by continued attempts to obtain high quality spectra from the cryolite-based melts. Several designs of spectrocell were constructed and tested with the final result being the invention of a what we believe to be a truly remarkable piece of laboratory apparatus: namely, a spectrocell capable of providing research grade spectra under extreme conditions. The cell will be described later. But first it is instructive to recount the other less successful designs that were tested and to report upon their attributes and shortcomings. All of the comments are in reference to measuring the Raman spectra of cryolite-based melts, i.e., fluoride chemistries.

The first cell consisted of single crystal sapphire tubing. The thought was that although sapphire is attacked by cryolite, the rate of attack would be slow enough to allow the measurement of the spectra of oxide-free fluoride melts. This proved not to be the case. Eventually we would learn that the rate of attack and the geometry of the cell would combine so as to magnify the presence of oxide in the melt even at very short times.

A second cell consisted of a crucible and hanging rod both of which were contained in an outer closed end fused quartz tube the top of which was fitted with the stainless steel cap used in the previous chloride studies. The crucible and rod were made of inert materials such as boron nitride or graphite. The idea was to hold the melt in the crucible which acted simply as a reservoir. For taking spectra the rod was immersed in the melt to form a pendant drop which was held above the crucible in sight of the window of the furnace for illumination by the incident laser. This arrangement had two problems. First, cryolite would not wet some of the rods. Secondly, the droplet's curved external boundary had a lens effect which threw the laser beam in unwanted directions uncontrollably and made focussing impossible.

A third cell consisted of a suspended platform onto which a droplet of melt sat. While wettability was not a problem the lens effect was.

A fourth cell was designed by experimenting with room temperature spectra of carbon tetrachloride. It was discovered that by flattening the droplet through compression i.e., by essentially squeezing the droplet between two plates, the droplet took the shape of a cylinder and the laser beam could be focused. Much experimentation resulted in the discovery of the optimal spacing between the plates to get the best shaped droplet.

The fifth and final cell is that shown in Figure 1. The main features are (1) the crucible into which a cross cut has been made half way through so as to form a horizontal gap and (2) the rod which acts as a ram to force the melt to rise to the point where it is visible in the gap. This exploits the features of the fourth cell but does so in a much more convenient and elegant manner. We have tested such spectrocells constructed of graphite and of boron nitride. The principal attribute of this cell is that we are able to see the melt without allowing it to make physical contact with any window material such as fused quartz or sapphire, both of which we now know will rapidly contaminate the melt with oxygen.

Figure 2 is the spectrum of pure cryolite taken in the spectrocell of Figure 1. The results are far superior to any achieved to date. Polarization settings are vertical in and vertical out. Of interest is the strong peak way out at 1463 cm^{-1} . Figure 3 is the same as Figure 2 with the exception that the polarization settings are horizontal in and vertical out. Note that the strong peak at around 600 cm^{-1} has completely disappeared which demonstrates full depolarization, something that should occur but could not be observed in the spectra obtained previously. There was no explanation for the peak at 1463 cm^{-1} at the time. Since then we have learned that this must have been a reaction product on the outer fused quartz container, probable due to attack by AlF_3 bearing vapor. We had never encountered this before because our cells had never been robust enough to permit us to conduct a experiment for such long times, except in the case of the sapphire mono-crystal which simply dissolved as Al_2O_3 in the melt.

Figure 4 shows the spectrum of a solution of 3 weight % Al_2O_3 in cryolite. There is no evidence of new peaks out around $800 - 900\text{ cm}^{-1}$ as suggested by some of the earlier literature. However, the peak near 600 cm^{-1} is somewhat attenuated. Figures 5 and 6 show the spectra of solutions of 5 and 10 weight % Al_2O_3 in cryolite, respectively. The attenuation of the peak near 600 cm^{-1} is stronger as the Al_2O_3 concentration increases in the melt. Further investigation is warranted to determine if a functional relationship can be established between the degree of attenuation and alumina concentration. If so, this would be the basis for a technique for on-line analysis of melt composition.

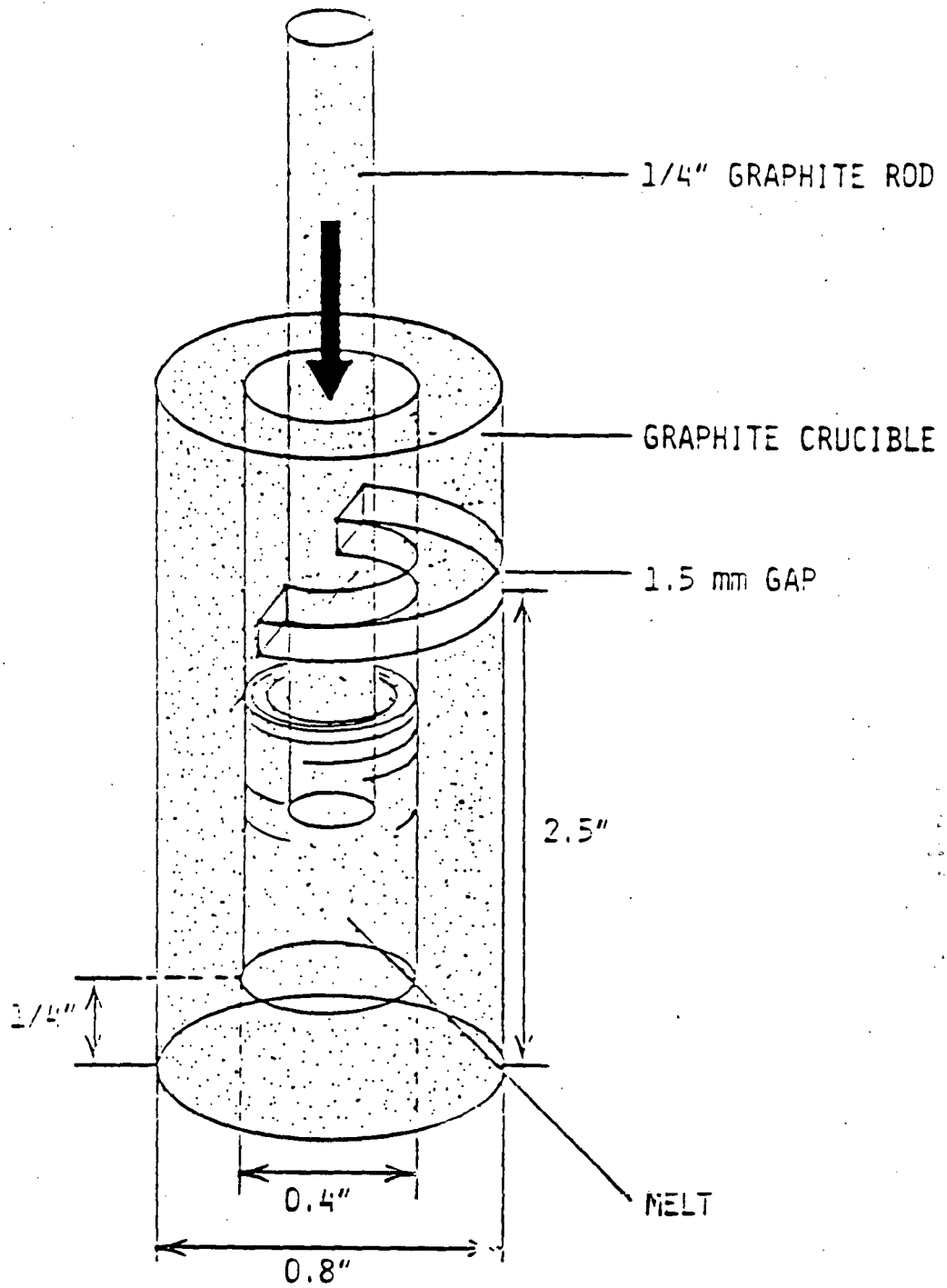


Figure 1. Raman spectrocell for corrosive melts

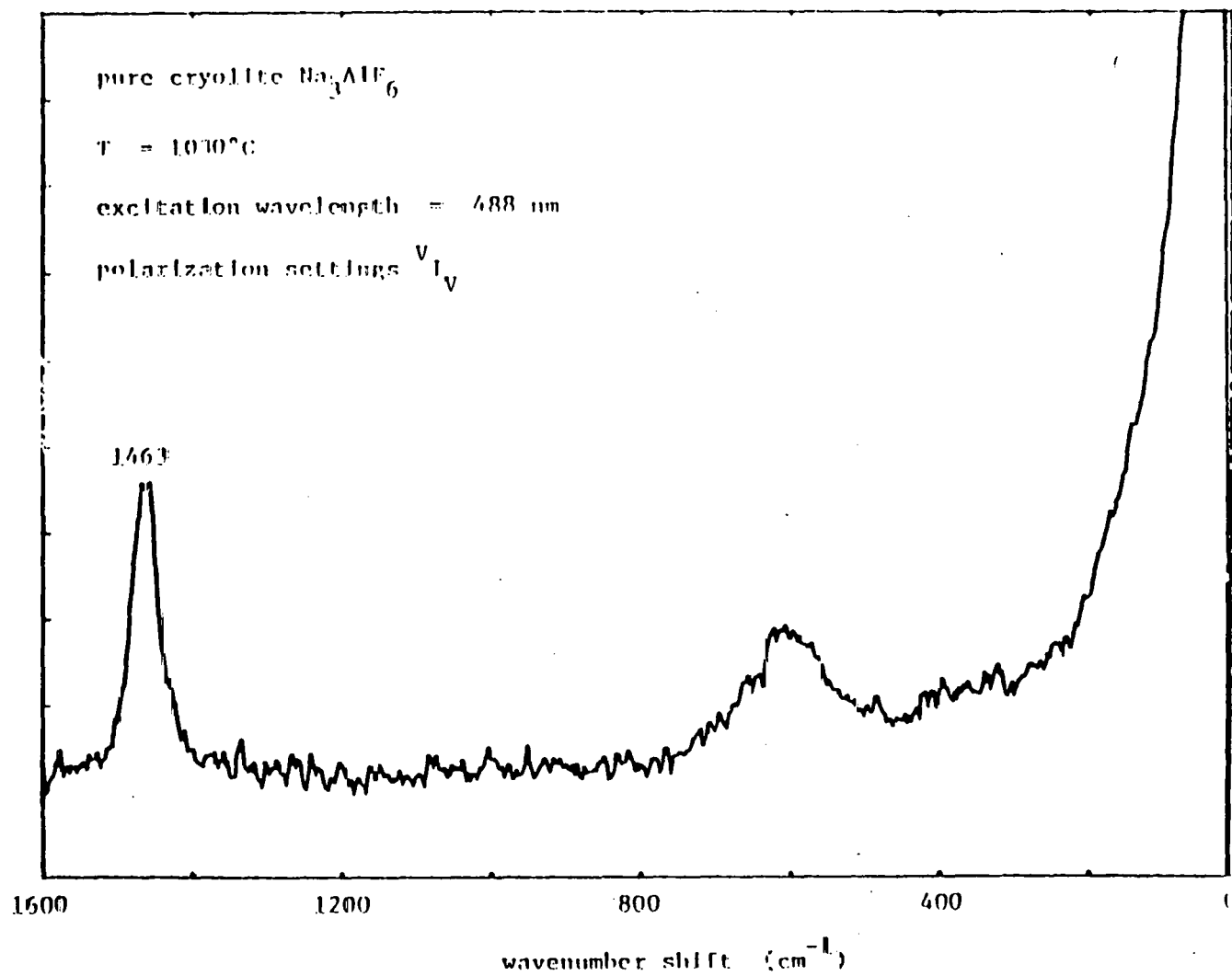


Figure 2. Raman spectrum of pure cryolite taken in new spectrocell.

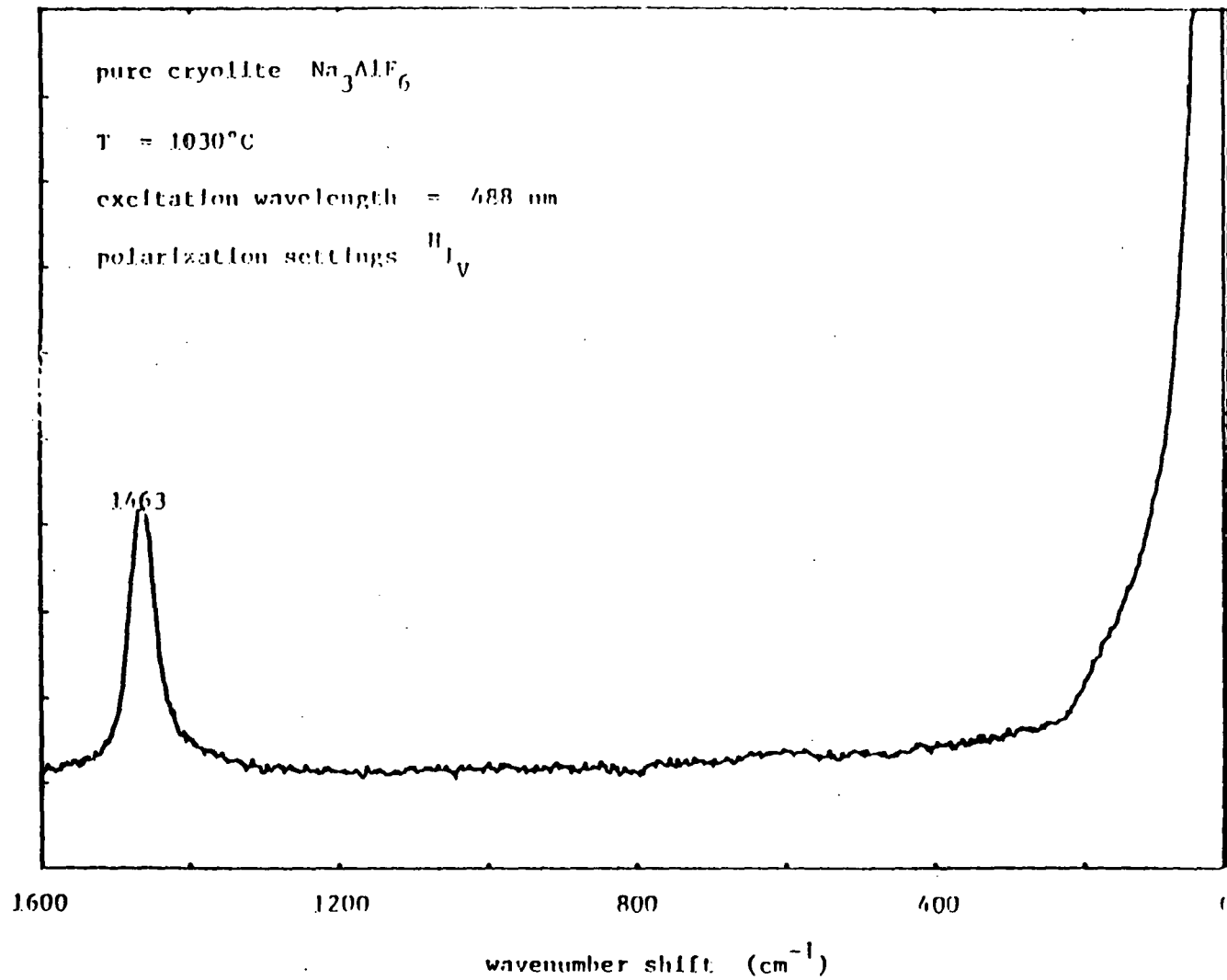


Figure 3. Raman spectrum of pure cryolite taken in new spectrocell.

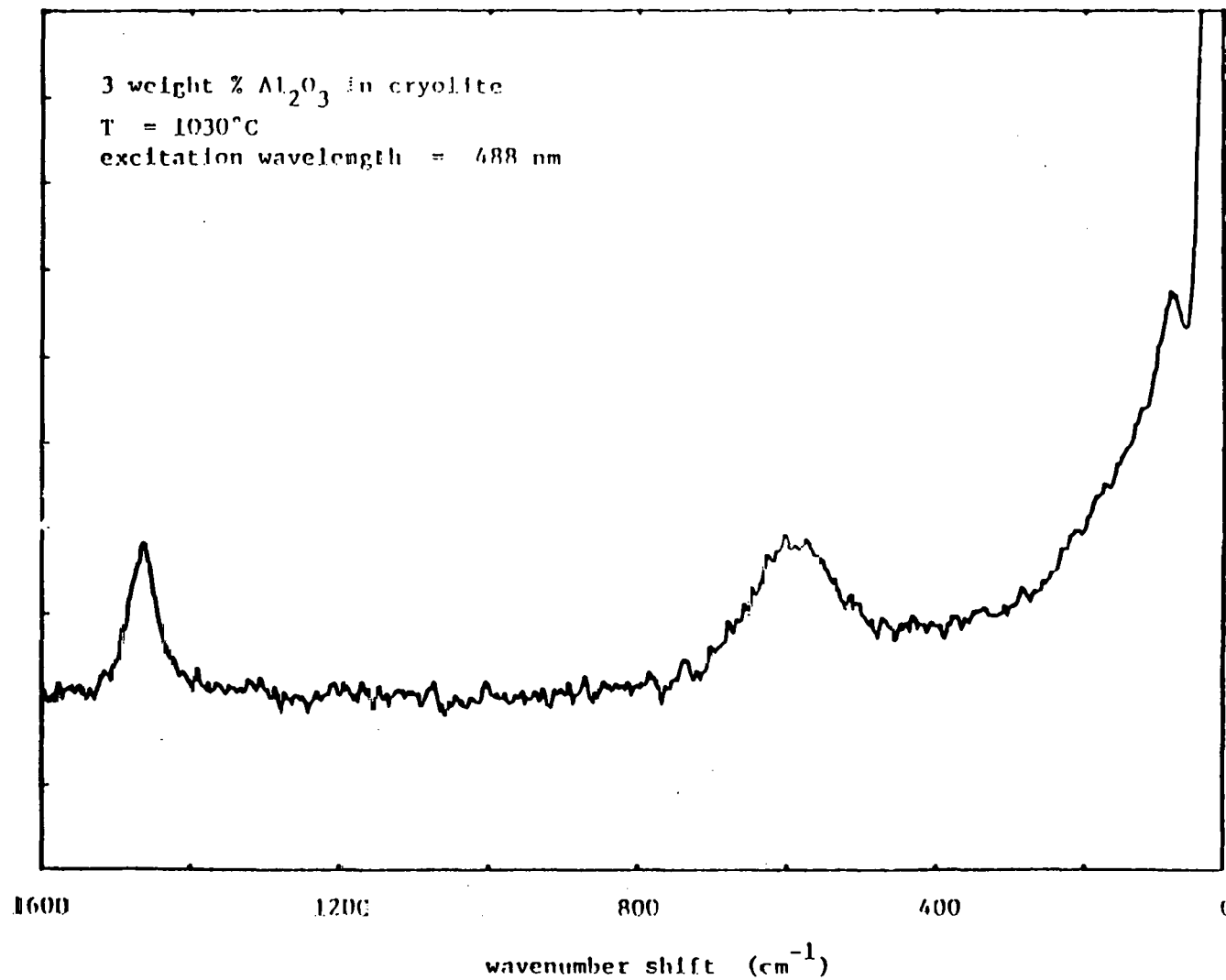


Figure 4. Raman spectrum of 3 wt % Al_2O_3 in cryolite.

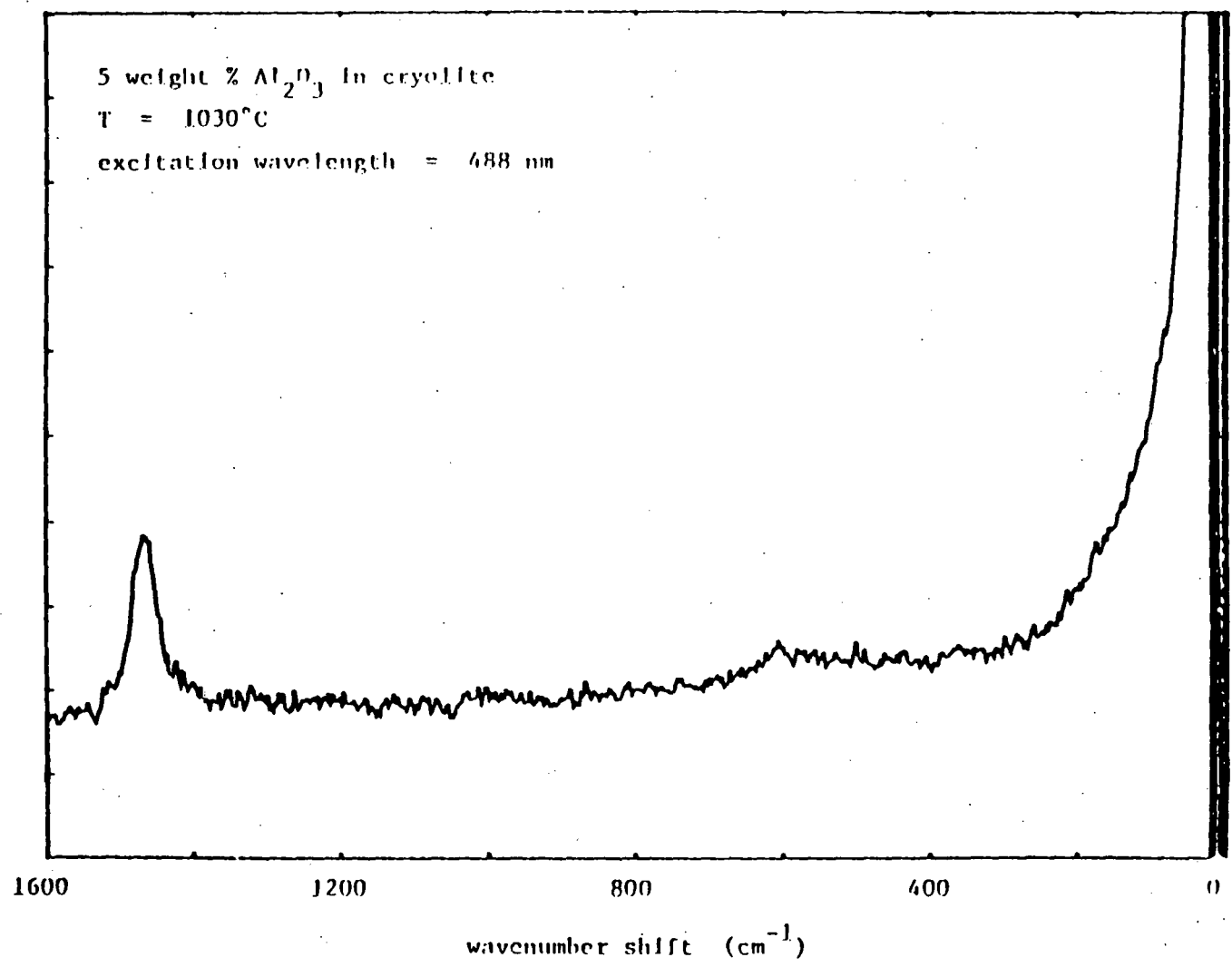


Figure 5. Raman spectrum of 5 wt % Al_2O_3 in cryolite.

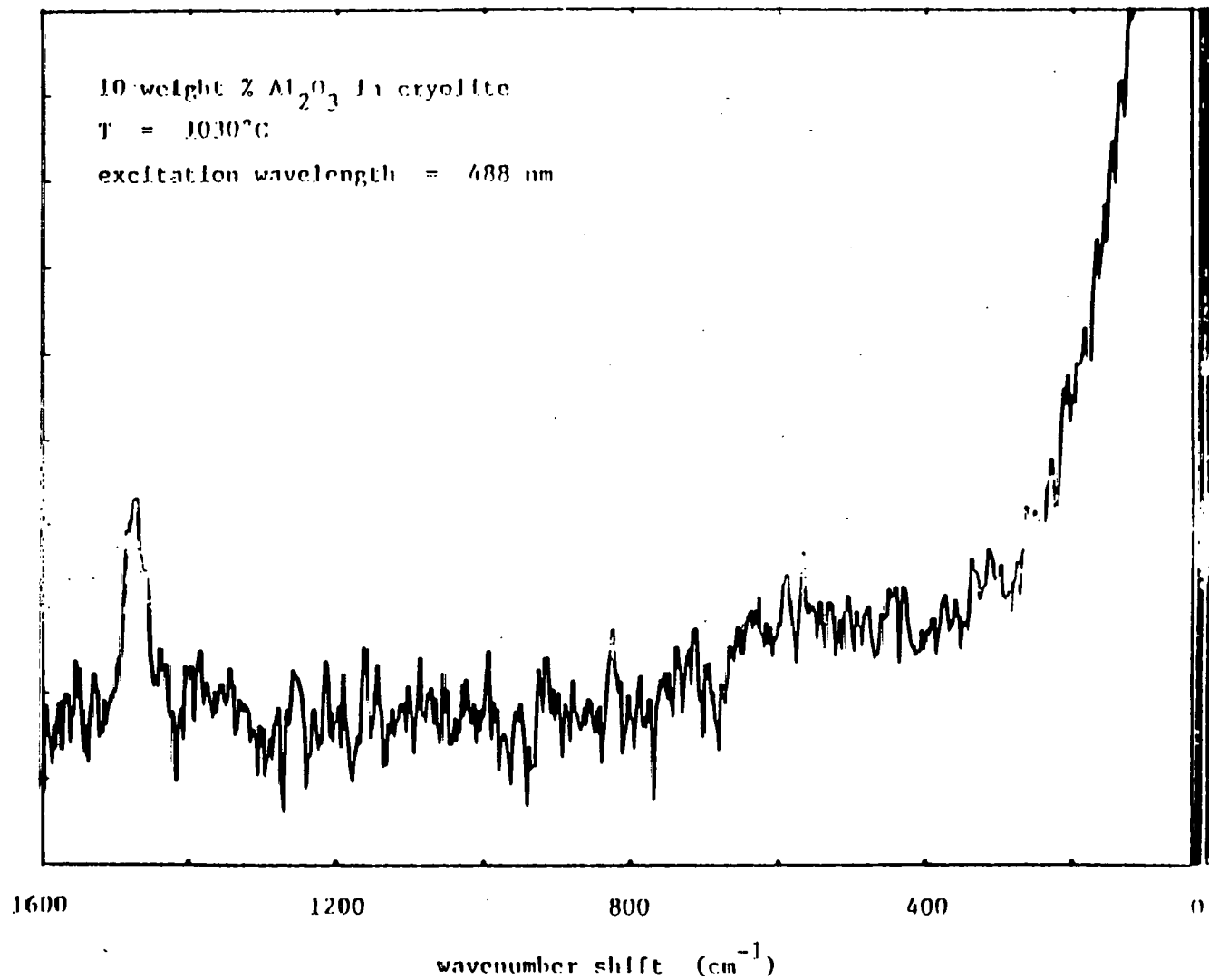


Figure 6. Raman spectrum of 10 wt % Al_2O_3 in cryolite.

APPENDIX E
EXCERPT FROM QUARTERLY PROJECT REPORT
DOE/CE/40545-24

EXCERPT FROM QUARTERLY PROJECT REPORT
DOE/CE/40545-24

Following is a discussion of research accomplishments from the quarterly project report DOE/CE/40545-24:

This quarter was marked by the taking of a large amount of data. The spectrocell described in the previous report, DE/CE/40545-23, proved to be a workhorse. The results will be described according to campaigns.

One set of experiments sought to determine whether Raman spectroscopy could reveal the state of chemical coordination in the fluoroaluminate complexes present in cryolite based electrolytes. A series of melts containing various ratios of AlF_3 and Na_3AlF_6 was studied to investigate how melt composition or, more specifically, bath ratio affects the complexing and coordination. The dominant reaction under these conditions is



which can also be thought of in terms of an acid-base equilibrium in which AlF_4^- acts as the acid and F^- acts as the base. Strictly speaking, the bath ratio is the ratio of NaF to AlF_3 by weight. Related to this is the cryolite ratio which is the ratio of NaF to AlF_3 on a molar basis.

Figure 1 shows the Raman spectrum of a melt containing AlF_3 and Na_3AlF_6 in a 1:1 mole ratio. The temperature of the melt was 870°C , and the excitation radiation had a wavelength of 488 nm. The spectrum is of superb quality. There are several reasons for this. First, the melts were of high purity due to our careful preparation procedures which involved premelting. Secondly, the spectrocell allowed us to avoid contaminating the melts during the course of taking the data. Thirdly, with the equipment modifications described previously, data processing was greatly enhanced in terms of our ability to do curve smoothing, plotting, analysis, etc. There are five peaks in Figure 1: 210 cm^{-1} dp, 330 cm^{-1} dp, 625 cm^{-1} p, 760 cm^{-1} dp, and 580 cm^{-1} p. The first four fit the pattern for a tetrahedrally coordinated complex, which in this case is obviously AlF_4^- . The peak at 580 cm^{-1} is on the shoulder of the major peak at 625 cm^{-1} and represents the major peak of pure cryolite. As such it is a representation of octahedral coordination as expected in AlF_6^{3-} .

Figure 2 shows the Raman spectrum of a melt containing AlF_3 and Na_3AlF_6 in a 3:4 mole ratio. The temperature of the melt was 890°C , and the excitation radiation had a wavelength of 488 nm. The same five peaks as those present in Figure 1 appear in Figure 2. However, in Figure 2 the peaks at 625 cm^{-1} and 580 cm^{-1} have nearly the same intensity. This is an indication that the change in bath chemistry had changed the relative populations of the AlF_4^- and AlF_6^{3-} species according to the reaction cited above. As the amount of cryolite in the bath increases, the line associated with AlF_6^{3-} intensifies.

Figure 3 shows the Raman spectrum of a melt containing AlF_3 and Na_3AlF_6 in a 1:2 mole ratio. The temperature of the melt was 890°C , and the excitation radiation had a wavelength of 488 nm. The results are much the same as those in Figure 2 with appropriate changes in the relative intensities of the peaks at 625 cm^{-1} and 580 cm^{-1} . In addition, there seems to be some broadening of the peak at 330 cm^{-1} .

Figure 4 shows the Raman spectrum of a melt containing AlF_3 and Na_3AlF_6 in a 1:4 mole ratio. The temperature of the melt was 990°C , and the excitation radiation had a wavelength of 488 nm. At this composition substantial changes are evident when the spectrum is compared to those in the previous figures. The peak at 625 cm^{-1} is barely visible, appearing in the shoulder of the peak at 580 cm^{-1} . Despite excellent curve smoothing it is evident that this spectrum is much noisier than the previous ones. This is in part due to the higher temperature of the measurement, 990°C , as compared to $870^\circ - 890^\circ\text{C}$.

Finally, just for reference, Figure 5 shows the Raman spectrum of a melt of pure cryolite, Na_3AlF_6 . The temperature of the melt was 1030°C , and the excitation radiation had a wavelength of 488 nm. The results are superb. The peak at 580 cm^{-1} is sharp. The peak at 380 cm^{-1} is clear. The depolarization is complete. Signal-to-noise is remarkable for a spectrum taken at a temperature of 1030°C in a 1:1 mole ratio.

A second set of experiments sought to determine whether Raman spectroscopy could reveal the state of chemical coordination in the fluoroaluminate complexes when oxygen was added to the melt. Actually, the work was prompted by the observation that with the new spectrocell, the main peak in pure cryolite was nearer 580 cm^{-1} than 535 cm^{-1} as had been previously measured in this laboratory (DE/CE/40545-15). It was thought that this was due to more accurate calibration of the spectrometer which in fact records intensity as a function of channel number rather than as a function of wavenumber. The mapping from channel number to wavenumber is done by calibration with a standard light source, typically the plasma lines of a neon light or the plasma lines of the Raman laser which has been purposely detuned. However, recalibration is unlikely to have been the cause for a shift of 45 cm^{-1} for this cryolite peak. A more plausible explanation is that the spectra obtained in the new spectrocell were truly those of the pure fluoride, while the spectra obtained earlier in the monocrystal sapphire cells had been contaminated with oxygen. To test this hypothesis a set of experiments was conducted in which the amount of alumina dissolved in cryolite was varied.

Figure 6 shows the Raman spectrum of a melt containing 11 weight percent Al_2O_3 in cryolite. The temperature of the melt was 1030°C , and the excitation radiation had a wavelength of 488 nm. Just as is the case with the fluoride spectra in Figures 1 through 5, the spectrum is of superb quality. At first glance, Figure 6 seems identical to Figure 5. However, in Figure 6 the main peak, which in Figure 5 appears at $\approx 580\text{ cm}^{-1}$, has shifted to $\approx 530\text{ cm}^{-1}$. As mentioned above, the spectra of pure cryolite measured in sapphire cells looked very similar to Figure 6 except that the signal-to-noise ratio of the earlier spectra was much poorer. Thus, it is clear that the presence of oxide in the melt is shown by the change in the position of

the main peak. The next question was, "Is there a functional relationship between oxygen content and wavenumber shift?" To answer this question a set of spectra was measured for a variety of melts of different oxygen content. In all cases the temperature of the melt was 1030°C and the excitation radiation had a wavelength of 488 nm.

Figure 7 shows the Raman spectrum of a melt containing 3 weight percent Al_2O_3 in cryolite. The same peaks as those present in Figure 6 appear in Figure 7. However, in Figure 7 the main peak is found at $\approx 552 \text{ cm}^{-1}$.

Figure 8, 9, 10, and 11 show the Raman spectra melts containing respectively, 5, 8, 13, and 15 weight percent Al_2O_3 in cryolite. The main peak shifts to lower values of wavenumber shift as the alumina concentration increases. However, once the alumina concentration reaches a certain value, there is no further change in wavenumber shift. This is an indication that the bath has become saturated with alumina, a fact detected in the Raman spectrum.

Figure 12 is a plot summarizing the data and showing the relationship between alumina concentration and wavenumber shift. It appears that there is a linear relationship between alumina concentration and wavenumber shift. Furthermore, the intersection of the two line segments occurs at a composition consistent with the known liquidus at the temperature of the measurements. These findings are very exciting as there are commercial implications of this discovery as well as implications for scientific research. Commercially, we are talking about an *alumina sensor*. Academically, do we now have a technique to measure noninvasively the solubility of metal oxides in cryolite? Imagine the consequences for inert anode studies. What about phase diagram determination?

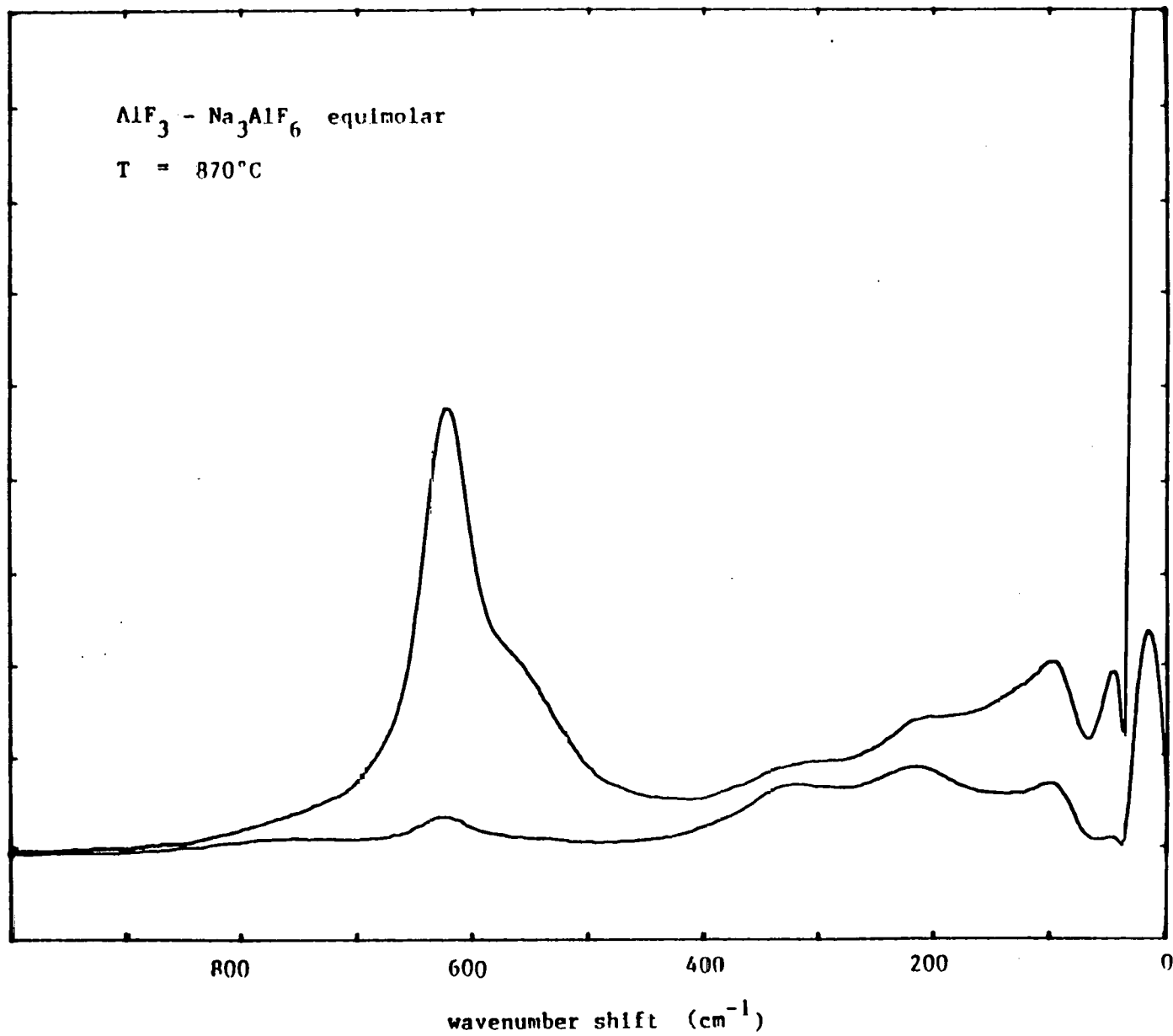


Figure 1. Raman spectrum of equimolar $\text{AlF}_3 - \text{Na}_3\text{AlF}_6$.

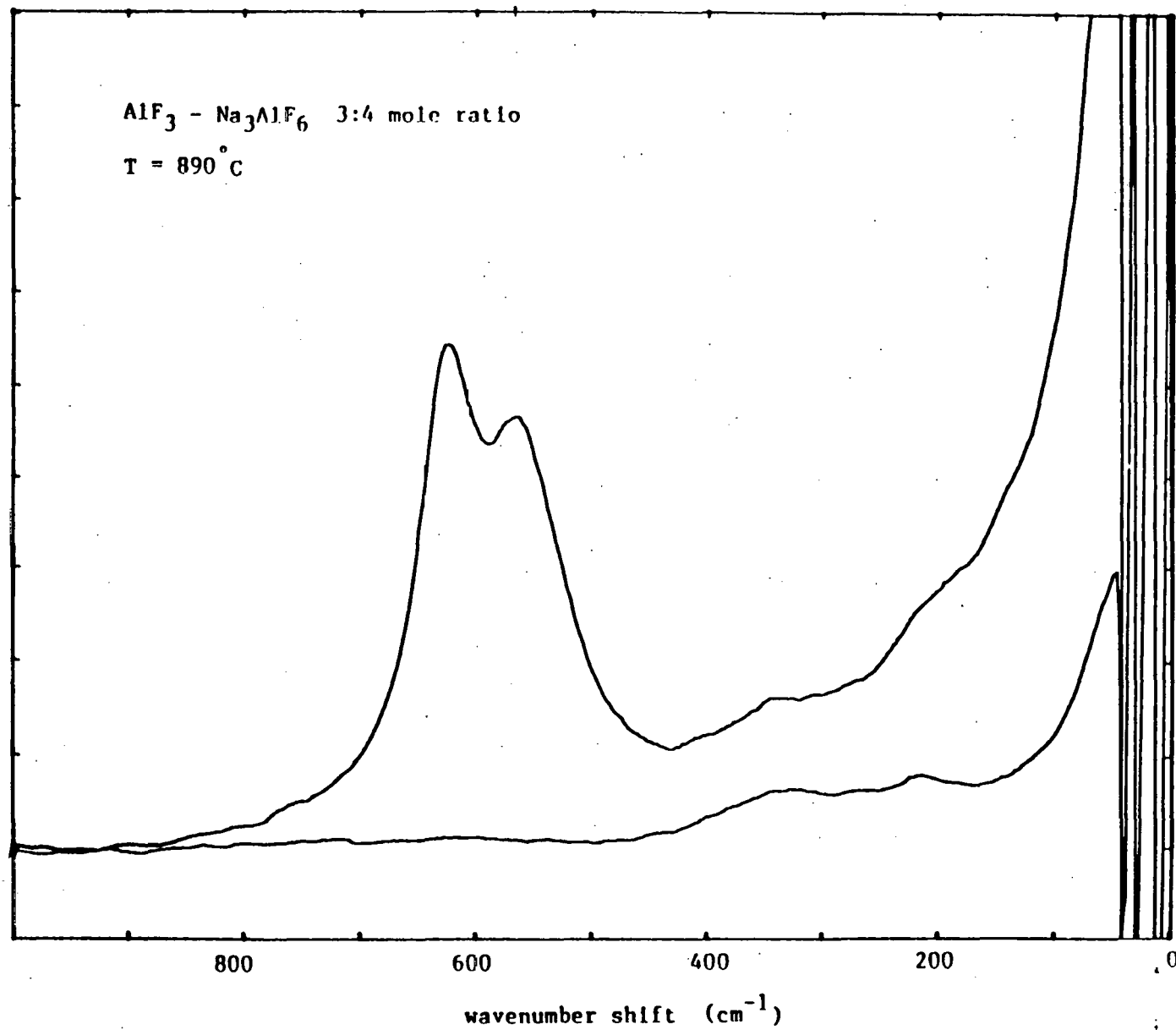


Figure 2. Raman spectrum of $\text{AlF}_3 - \text{Na}_3\text{AlF}_6$ in a 3:4 mole ratio.

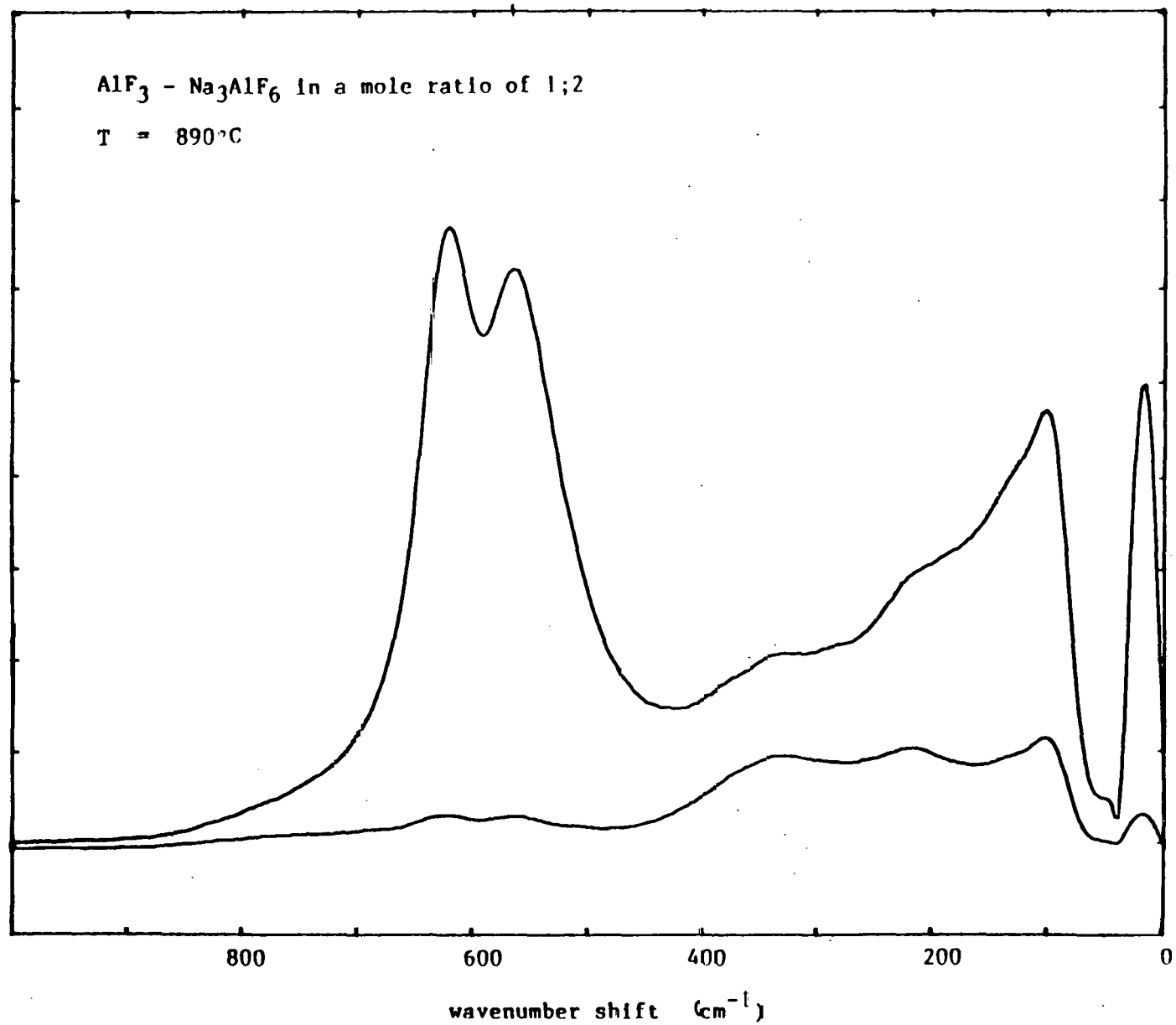


Figure 3. Raman spectrum of $\text{AlF}_3 - \text{Na}_3\text{AlF}_6$ in a 1:2 mole ratio.

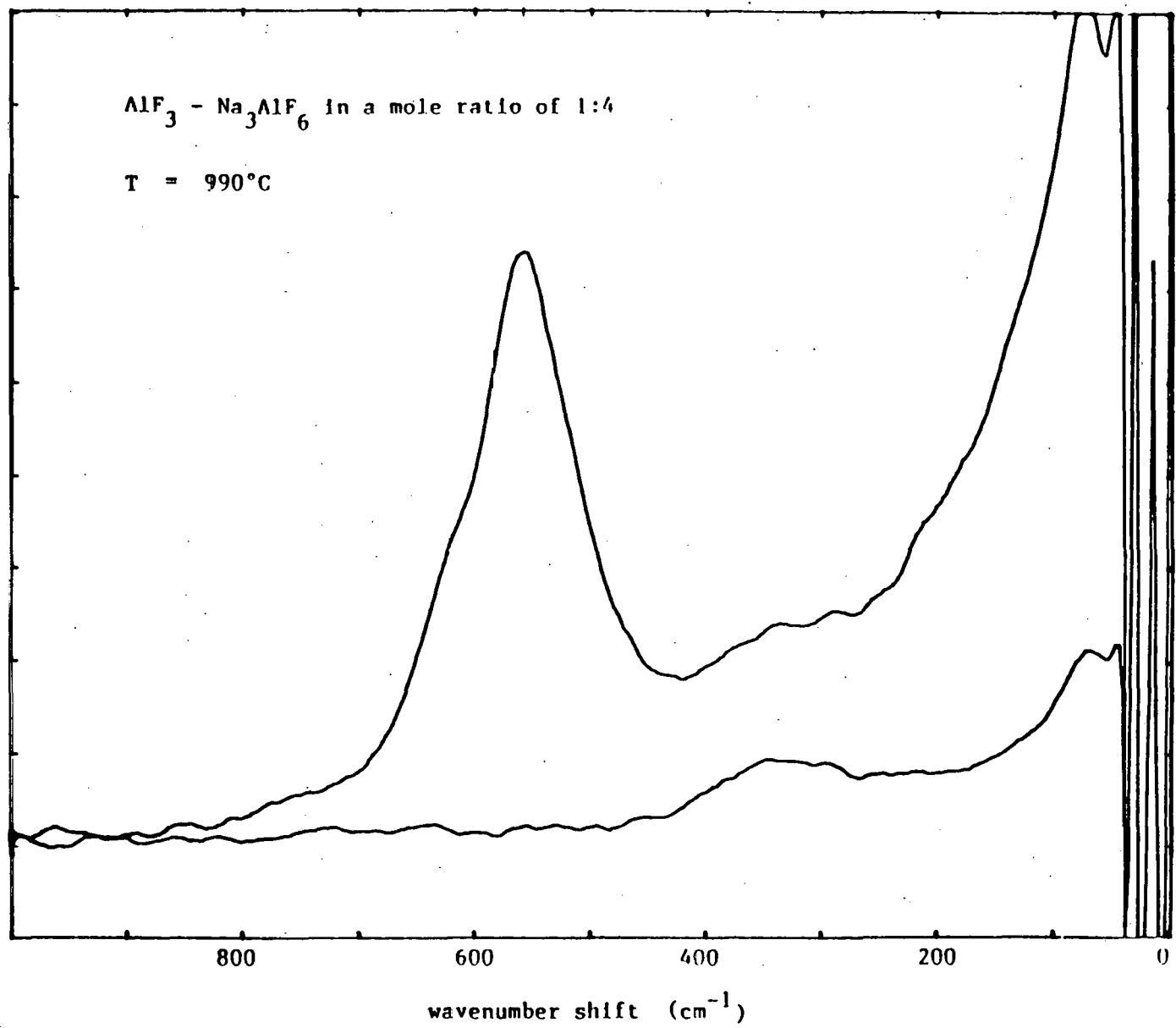


Figure 4. Raman spectrum of $\text{AlF}_3 - \text{Na}_3\text{AlF}_6$ in a mole ratio of 1:4.

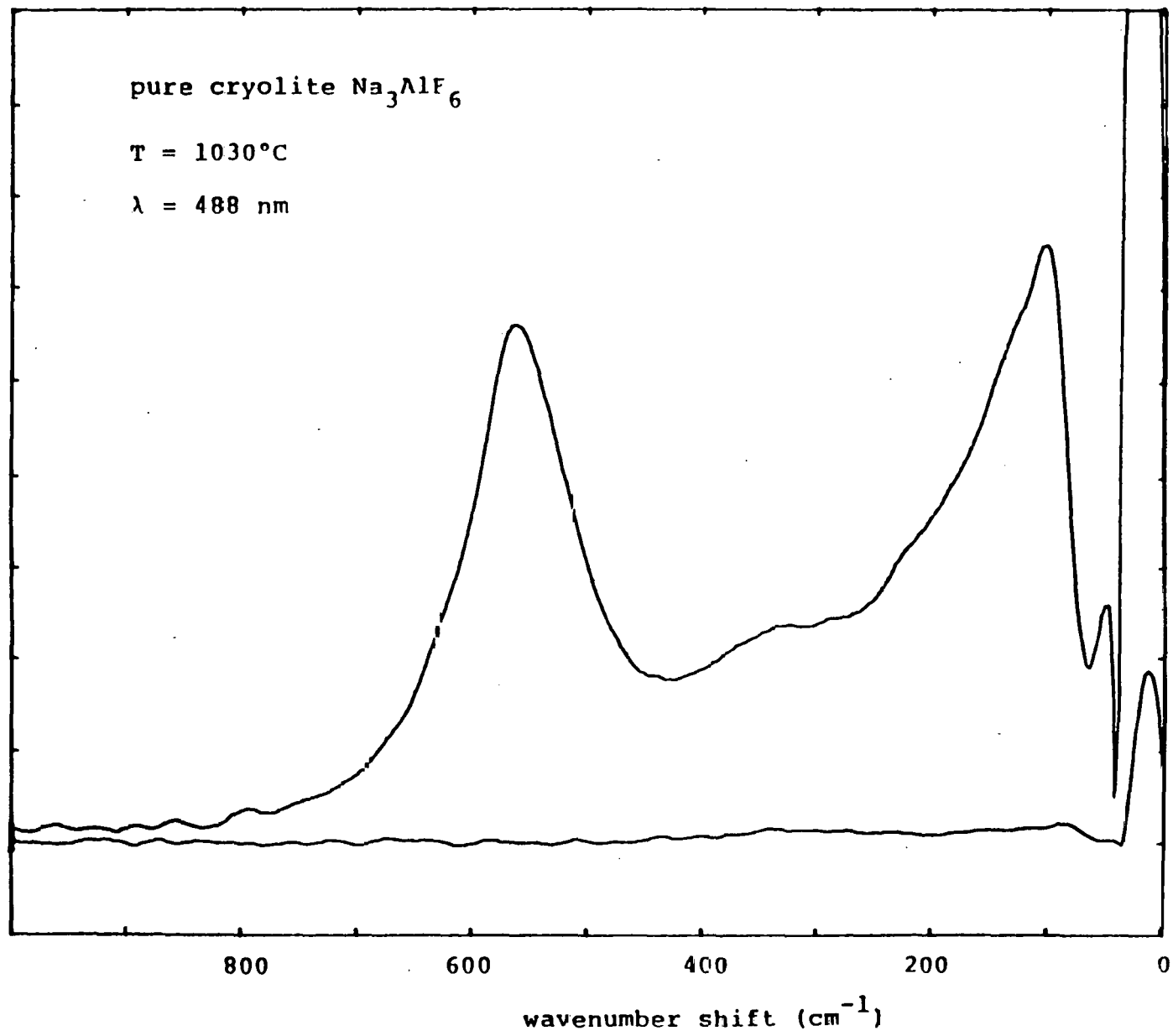


Figure 5. Raman spectrum of pure cryolite.

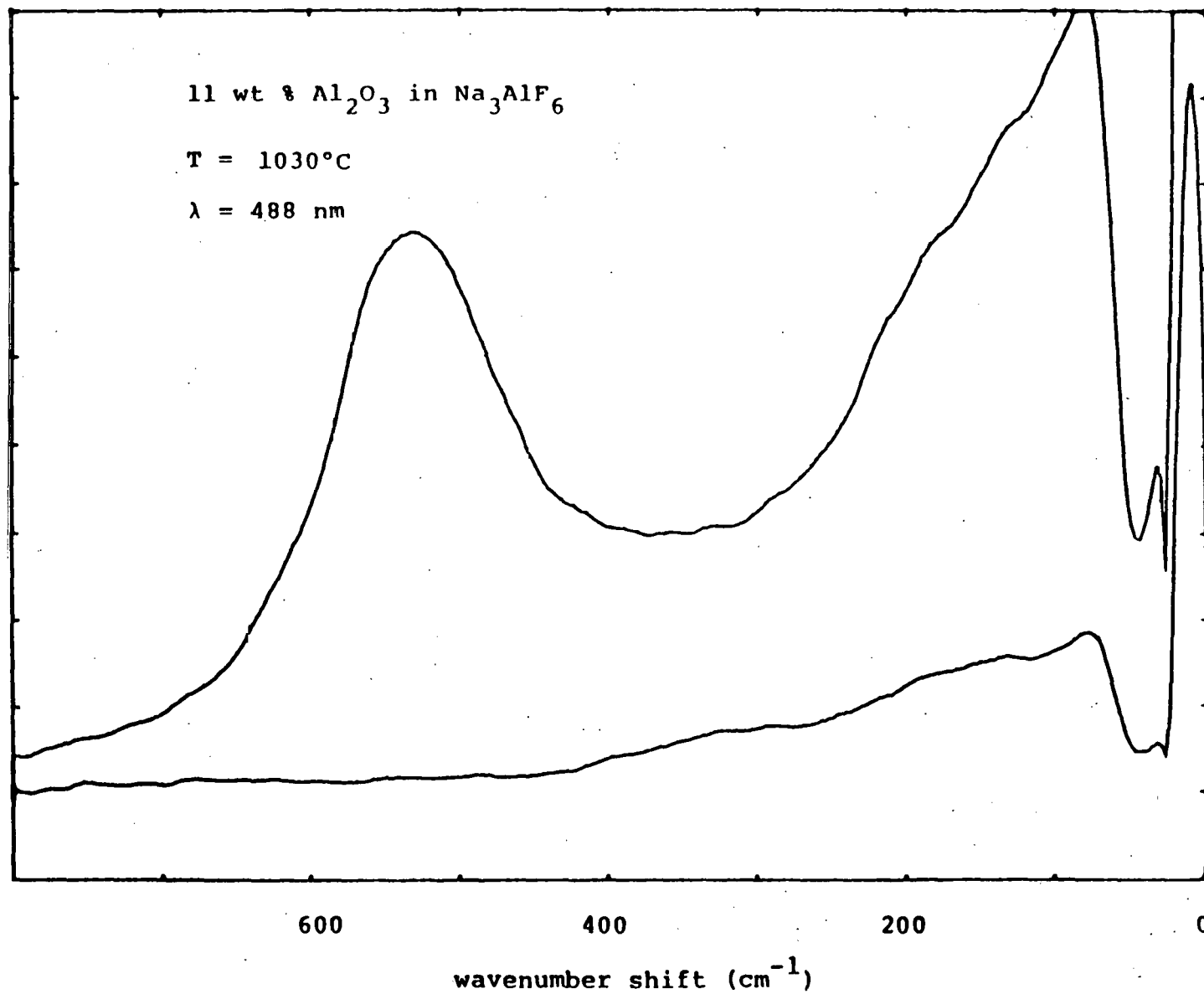


Figure 6. Raman spectrum of cryolite - 11 weight per cent alumina.

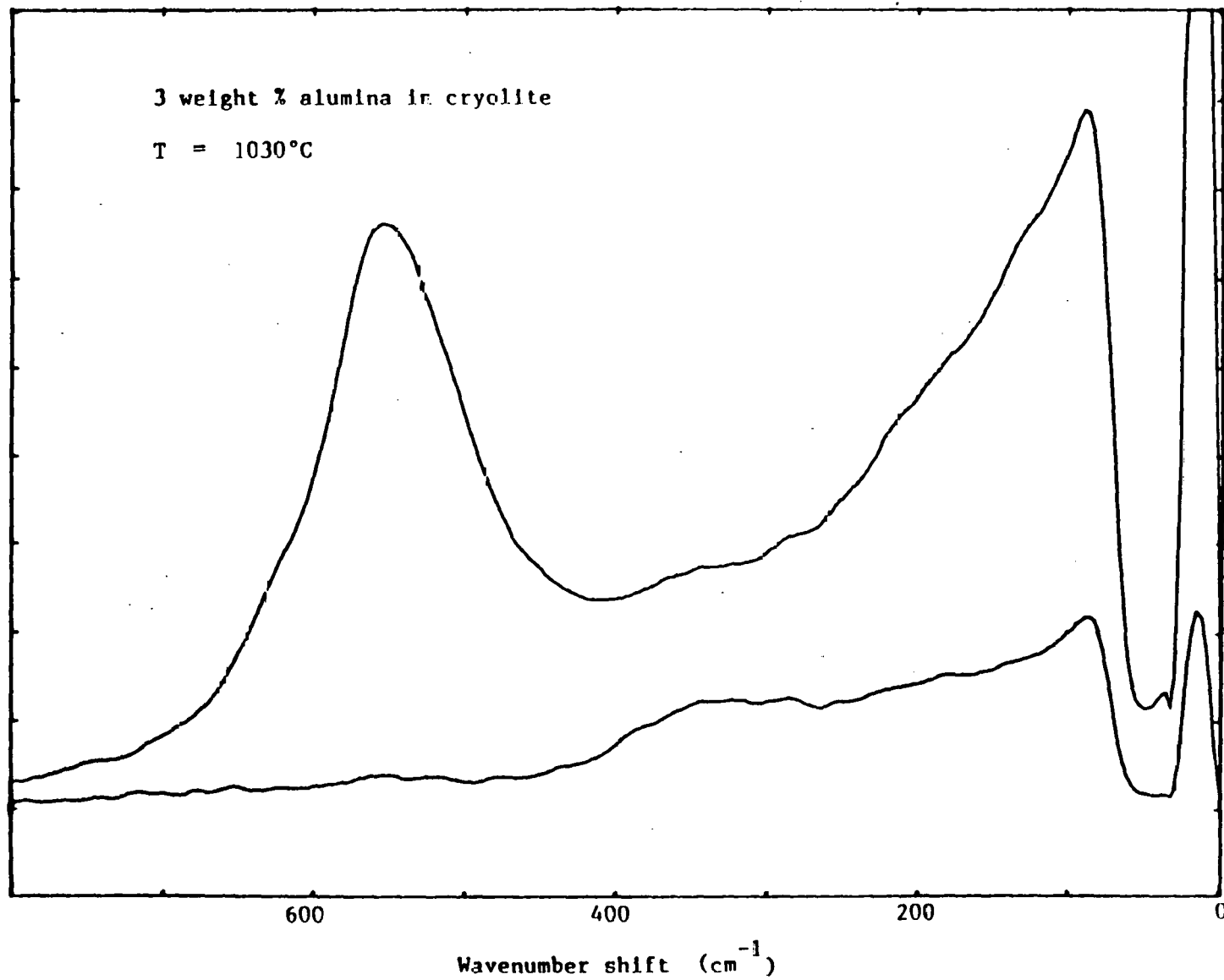


Figure 7. Raman spectrum of 3 wt % alumina in cryolite.

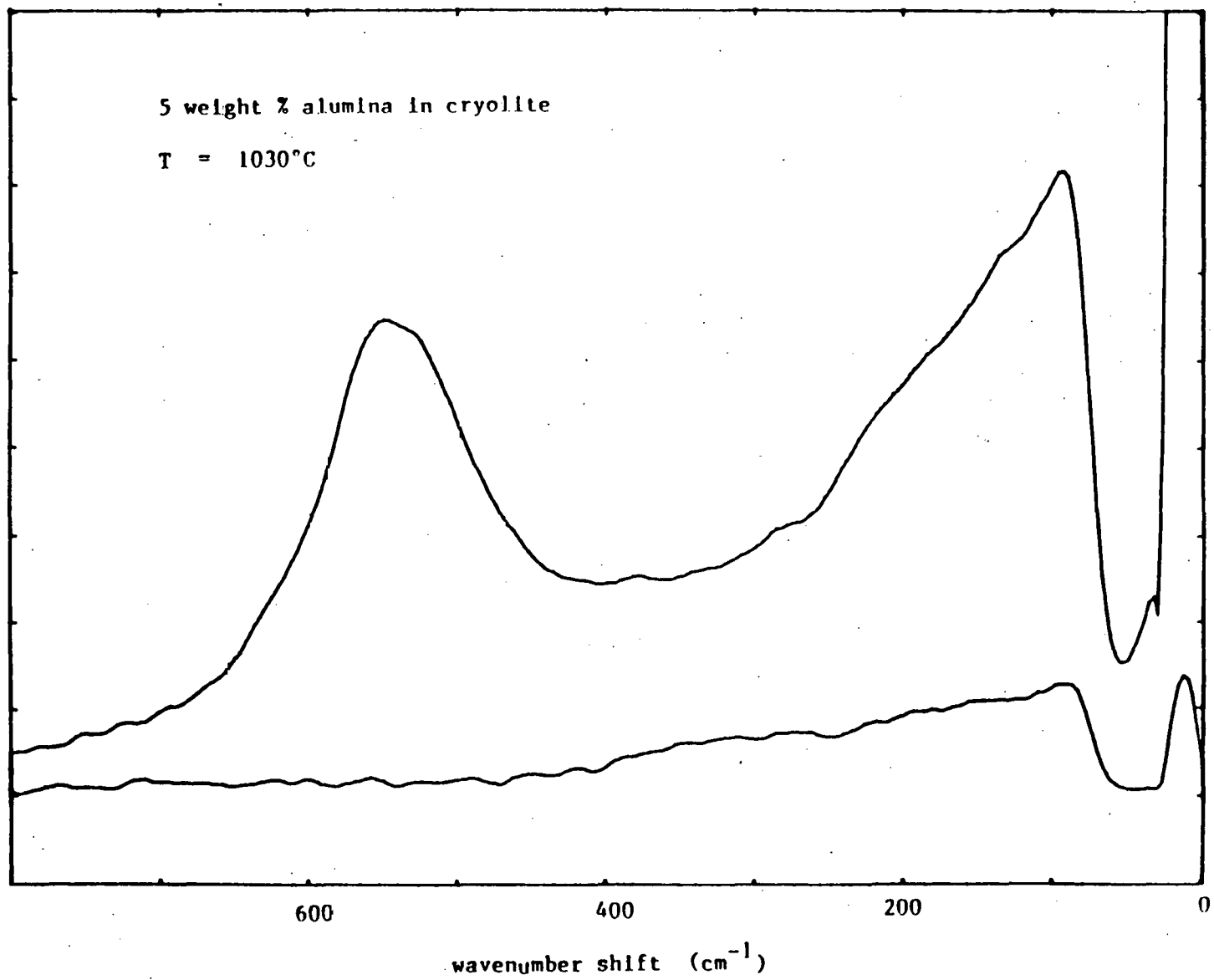


Figure 8. Raman spectrum of 5 wt % alumina in cryolite.

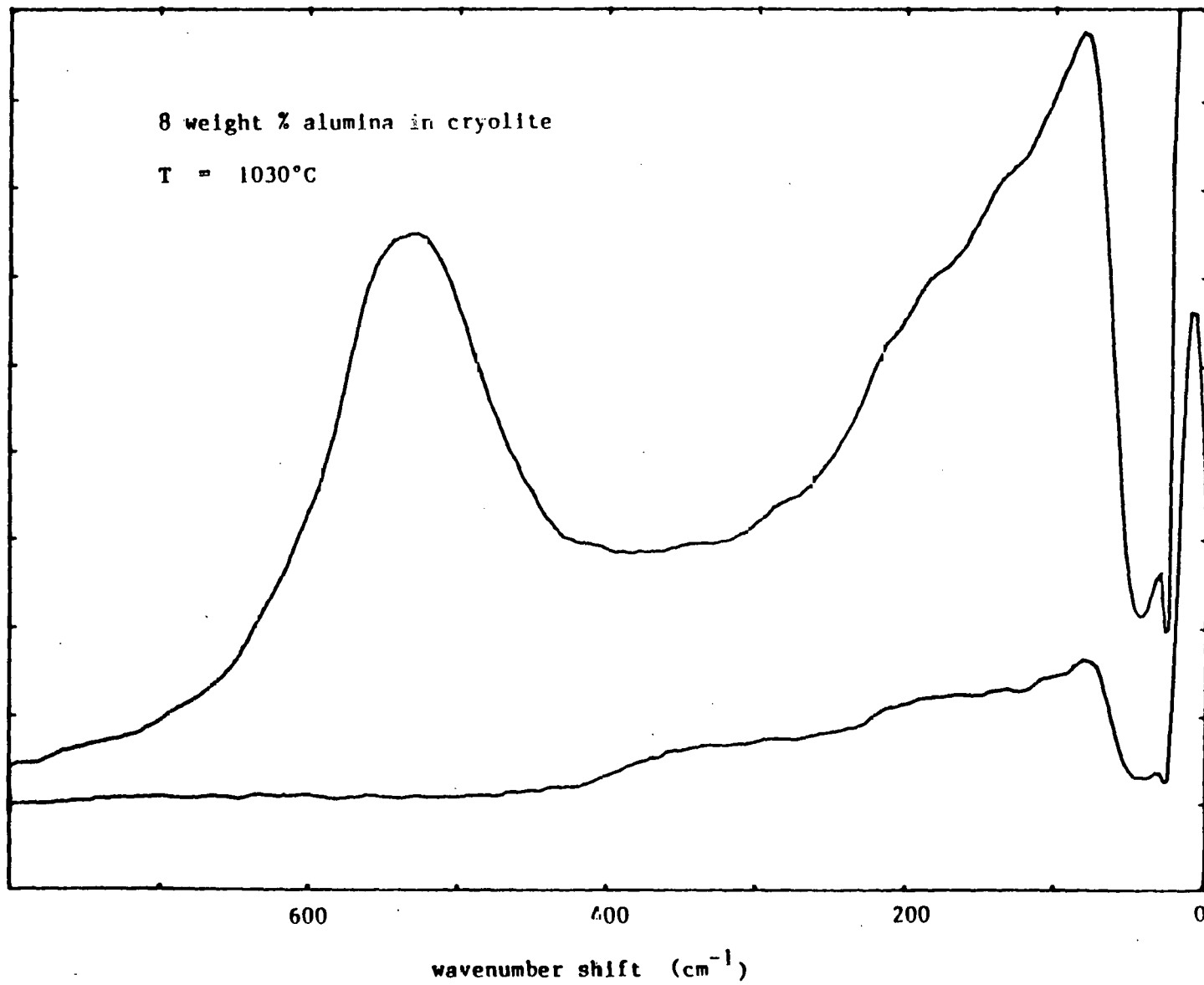


Figure 9. Raman spectrum of 8 wt % alumina in cryolite.

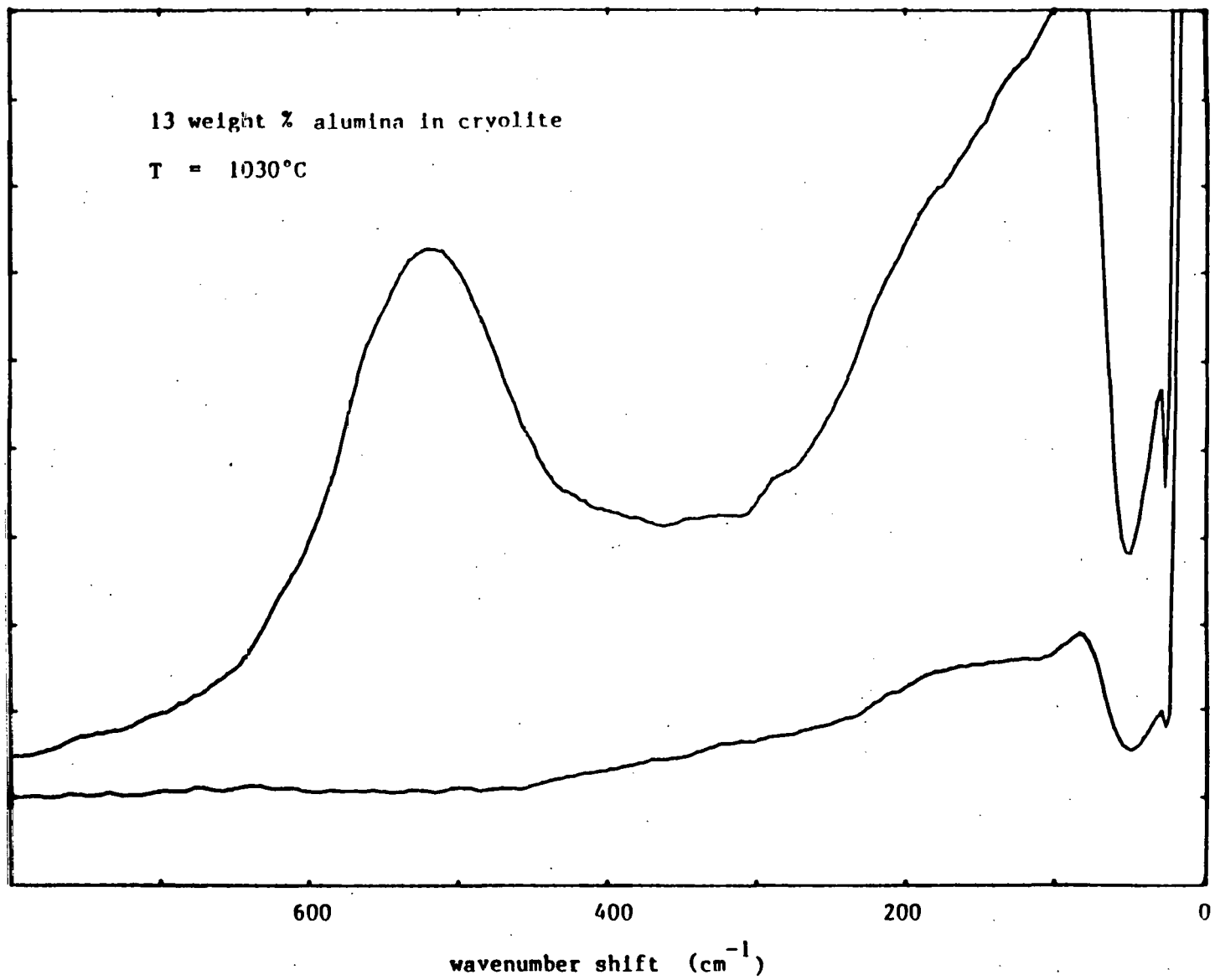


Figure 10. Raman spectrum of 13 wt % alumina in cryolite.

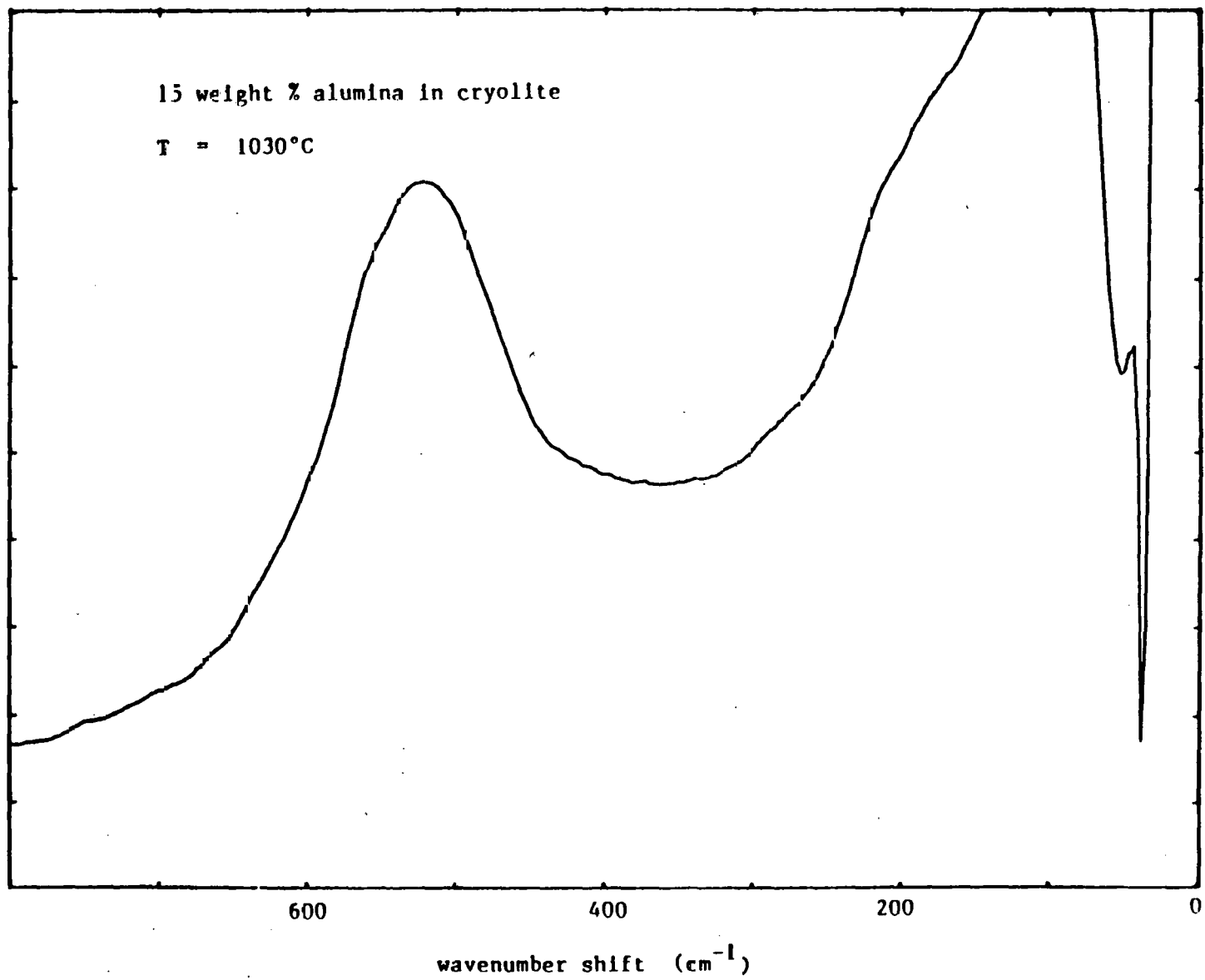
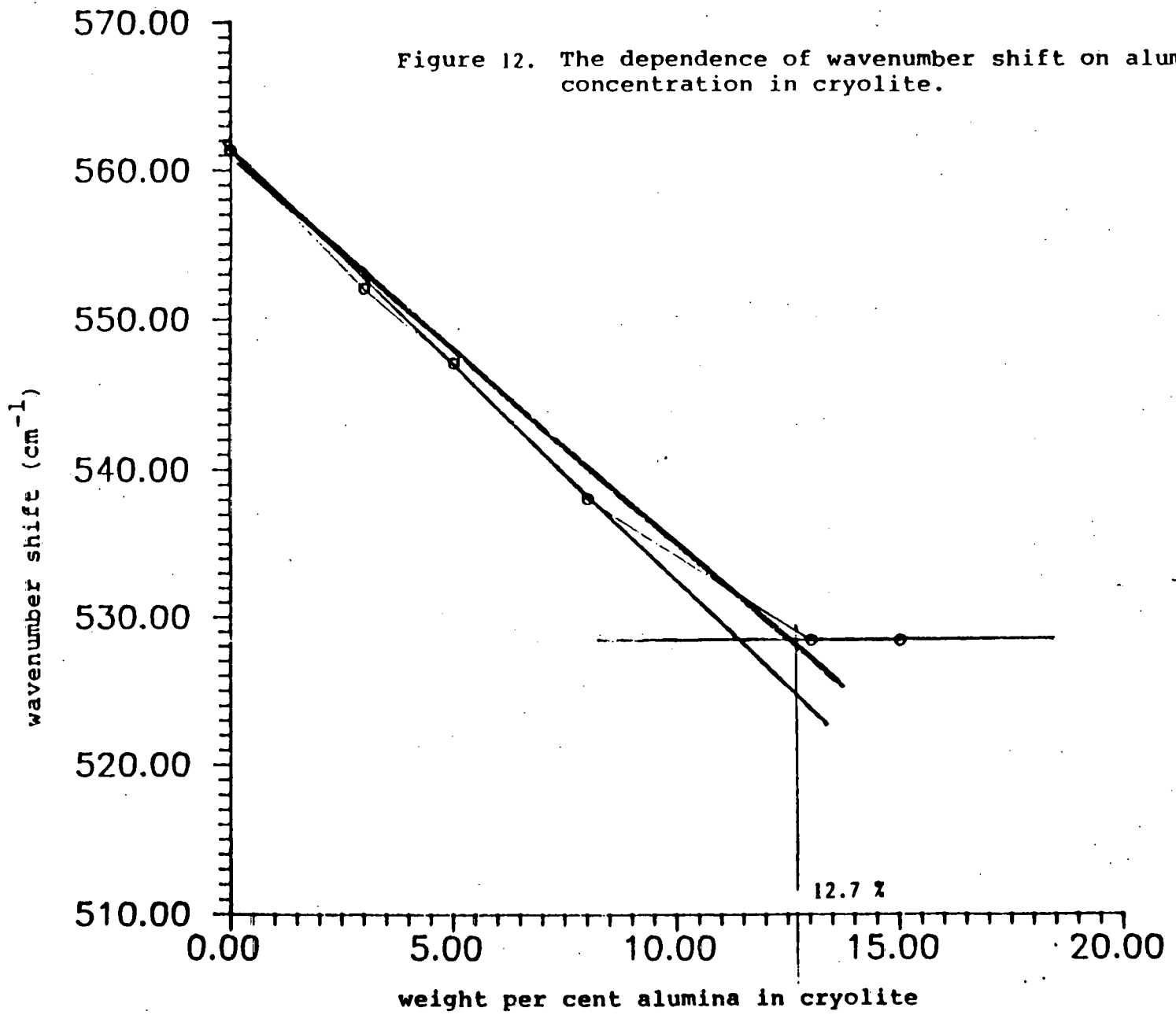


Figure 11. Raman spectrum of 15 wt % alumina in cryolite.

Figure 12. The dependence of wavenumber shift on alumina concentration in cryolite.



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DIAGNOSIS OF SOURCES OF CURRENT INEFFICIENCY IN INDUSTRIAL MOLTEN
SALT ELECTROLYSIS CELLS BY RAMAN SPECTROSCOPY

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