Growth of solid electrolyte from the melt under microgravity

A.Popov, I.Kostadinov, M.Mateev, A.Alexandrov,
L.Regel, N.Baturin

$RbAg_4J_5$

THIS IS THE FIRST TECHNOLOGICAL EXPERIMENT FOR CRYSTAL GROWTH OF SUPERIONIC MATERIALS IN MICROGRAVITY CONDITIONS. IT WAS PERFORMED ON THE BOARD OF THE SOVIET SPACE STATION MIR DURING THE JOINT SOVIET-BULGARIAN FLIGHT WITHIN THE SHIPKA PROGRAM USING THE CZECHOSLOVAKIAN CSK-1 EQUIPMENT.THE AIM OF SPACE EXPERIMENT WAS TO AVOID THE INFLUENCE OF SEGREGATION PROCESS DUE TO ATOMIC WEIGHT DIFFERENCES AND TO INVESTIGATE THE INFLUENCE OF MICROGRAVITY CONDITIONS ON THE CRYSTAL STRUCTURE.IN THE END IT WAS IMPORTANT TO OBTAIN A CRYSTAL OF $RbAg_4I_5$ IN THE SPACE FOR DEVICE APPLICATION.

It is well known that this material is the best room temperature super ionic conductor (1-5). Monocrystals of $RbAg_4I_5$ exist in three crystallografic modifications: α, β, γ with successive change from one to another as the temperature decreases (T_1=209K, T_2=122K). The low temperature γ-phase has a trigonal crystal lattice and it was wide gap semiconductor with E_g=3.34 eV. At 122K a first order transition occurs to the rombohedral β-phase which is an ionic conductor (the conductivity increases by a factor of 100). At higher temperature -209K a second order transition occurs to the cubic α-phase with superionic conductor properies and the conductivity increases by a factor of 10. High conductivity, and thus, applicability of this crystal are caused by disorderd position of Ag ions in the crystal cell, and the extent of disordering increases in transition from low temperature to high temperature phase.

ELEMENTS OF THE CRYSTAL STRUCTURE OF THE CUBIC α-PHASE $RbAg_4I_5$ (CELL PARAMETER a = 11.24 Å, SYMMETRY CLASS m3m) ARE SHOWN IN FIG.1.

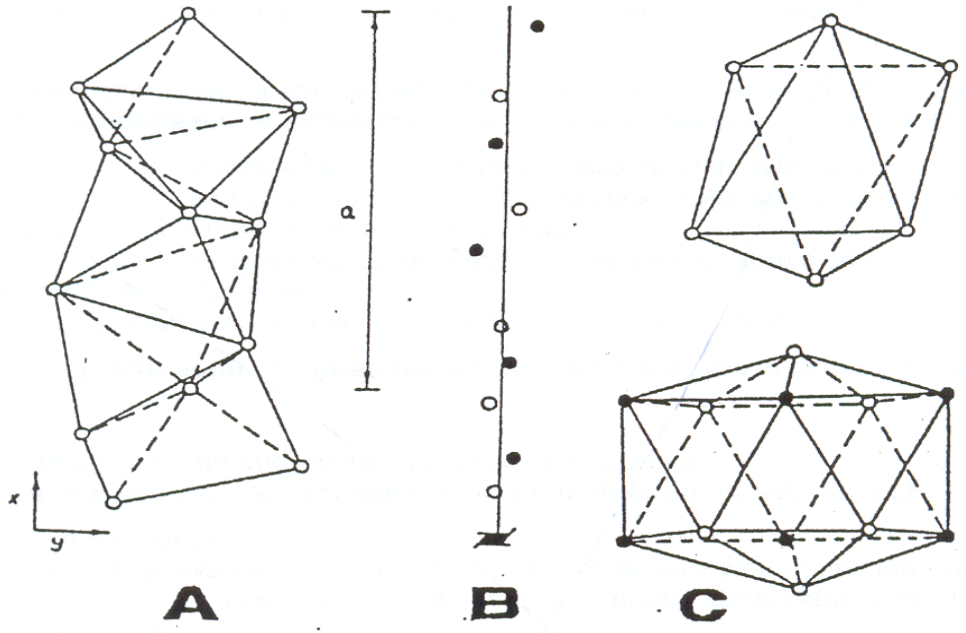


Fig.1. Elements of crystal structure of cubic α-phase $RbAg_4I_5$

A - COMBINATION OF Rb CO-ORDINATION TETRAHEDRONS OF CRYSTAL STRUCTURE

B - SITUATION OF CATHIONS M(1) AND M(2) ALONG THE 4 AXIS

C - TWO TYPES OF Rb CO-ORDINATION : 1 - OCTAHEDRON , 2 - ICOSAHEDRON

● - 8c POSITION ; ○ - 12D POSITION

POLYHEDRONS WITH JOINT BORDERS FORM CANALS OF CONDUCTIVITY ALONG 4_1 AXIS. COMBINATION OF THIS CANALS GENERATE THE THREE - DIMENTIONAL CONDUCTIVITY OF THE CRYSTAL.

MANY AUTHORS HAVE GIVEN MUCH CONSIDERATION TO ANALYSIS OF ALL THREE PHASES OF THIS CLASSICAL SUPERIONIC CONDUCTOR.THEY HAVE CONCLUDED THAT AN ADDITIONAL PHASE TRANSITION IS EXISTING AT LOW TEMPERATURE.THIS CONCLUSION WAS BASED ON THE ANALYSIS OF EXITONS AND IR SPECTROSCOPIC DATA.THUS, 4 MODIFICATIONS OF THE SEMICONDUCTING γ-PHASE ARE EXISTING, AS IT IS SHOWN IN FIG.2.

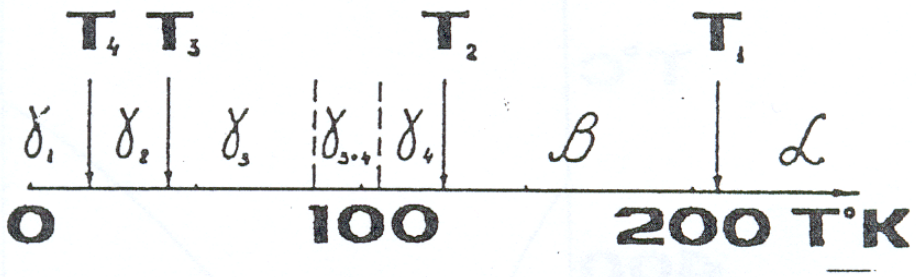


Fig.2. Scheme of phase transitions in $RbAg_4I_5$

T_1 – SECOND-KIND TRANSITION ; T_2 – FIRST-KIND TRANSITION ;

T_3 – SECOND-KIND TRANSITION ;

HOWEVER, THE SCIENTIFIC CONCLUSIONS WERE AMBIGUEOUS, SINCE THE $RbAg_4I_5$ CRYSTAL PROPERTIES DEPEND STRONGLY ON THE GROWTH CONDITIONS. SO, FOR THE FURTHER PROGRESS IT WAS ESSENTIAL THAT RALATIVELY LARGE STRUCTURALLY PERFECT CRYSTALS BEING THERMODINAMICALY EQUILLIBRIUM , SHOULD BE GROWN.

VARIOUS METHODS EXIST TO PRODUCE MONOCRYSTALS OF THIS COMPOUND. ONE OF THEM IS THE GROWTH FROM A SOLUTION OF ACETONE. THIS IS A VERY SLOW PROCESS AND THEREFORE THE RESULTING CRYSTALS ARE SMALL (2-3 MM). ANOTHER POSSIBILITY IS THE CHOKCHRALSKI METHOD WHICH ALSO HAS DISADVANTAGES. A THIRD METHOD IS BASED ON THE PHASE DIAGRAM OF THE QUASI-BINARY SYSTEM AgI-RbI, WHICH IS SHOWN IN FIG.3

THERE EXISTS A DEEP EUTECTIC REGION AT 198°C WITH ABOUT THE SAME RATIO OF COMPONENTS AS IN THE CRYSTAL WHICH CAN BE USED FOR THE LOW TEMPERATURE CRYSTALLIZATION FROM THE MELT. WE HAVE USED THIS METHOD FOR OUR CRYSTAL GROWTH EXPERIMENTS OF $RbAg_4I_5$ UNDER MICROGRAVITY.

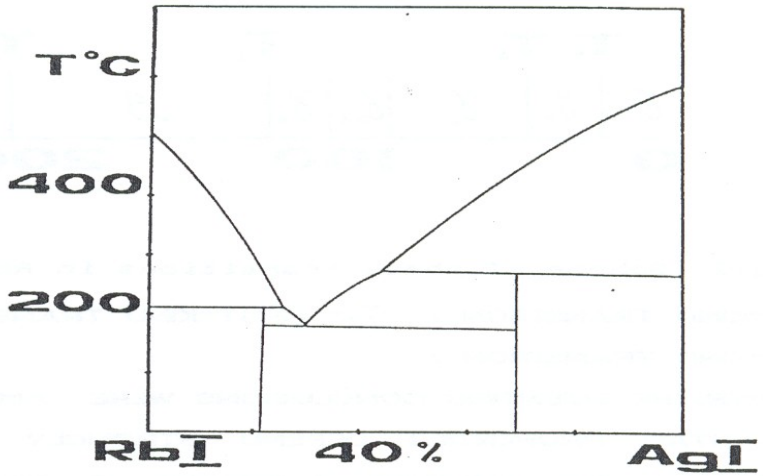


Figure 3. Phase diagram of RbI + AgI system (Ref. 2). Deep eutectic near the molar ratio 4 : 1. If the temperature is more than 228°C (melting point of $RbAg_4I_5$) - the system 25% RbI + 75% AgI is the melt, if the temperature is less - the system became the crystal $RbAg_4I_5$.

Fig.3. Phase diagram of RbI-AgI system

Deep eutectic is near the molar ratio 4 :1. If the temperature is more than 228 °C (melting point of $RbAg_4I_5$) the system (25% RbI + 75% AgI) is the melt.If the temperature is less- the system transforms in the crystal of $RbAg_4I_5$.

The crystals were produced in the microgravity conditions with the melt composition RbI and AgI 1:4 molar ratio which was placed in an evacuated quartz ampule.The ampule shape was chosen so that an increased probability of monocrystal seed production in microgravity is higher.A quartz stopper was soldered to the ampule rear part to prevent from possible melt spreading. Before the experiment the melt was homogenized directly in the ampule during 48 hours.The cross-section of the ampoule is schematically shown in Fig.4.

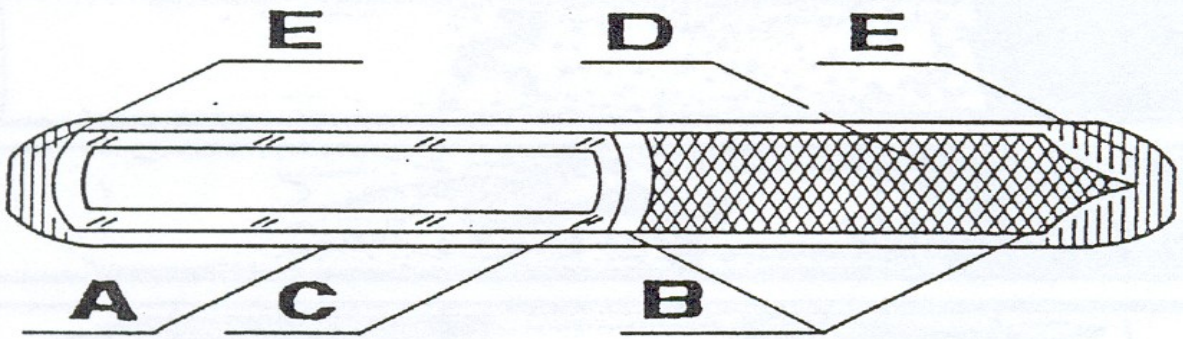


Fig.4. Construction of the ampoule for space experiments

A – STEEL CAPSULE FOR CSK-1 ; B – QUARTZ AMPOULE

C – QUARTZ STOPPER ; D – EXPERIMENTAL MATERIAL ;

E – SPECIAL WADDING

DIAGRAM OF THIS QUASI-BINARY SYSTEM. THE CSK-1 EQUIPMENT HAS 5 SEPARATED HEATERS (A,B,C,D,E) AND THE TEMPERATURE PROFILE WAS THE FOLLOWING : HEATER A – 290 °C , B – 240 °C , C – 0 °C , D – 145 °C , E – 165 °C . THIS YELDS TWO TEMPERATURES PLATEAUX ON THE THERMAL PROFILE ABOVE AND BELOW THE $RbAg_4I_5$ MELTING POINT (228 °C), AND AN APPROPRIATE TEMPERATURE GRADIENT 10 °C/cm IS SHOWN IN FIG.5.

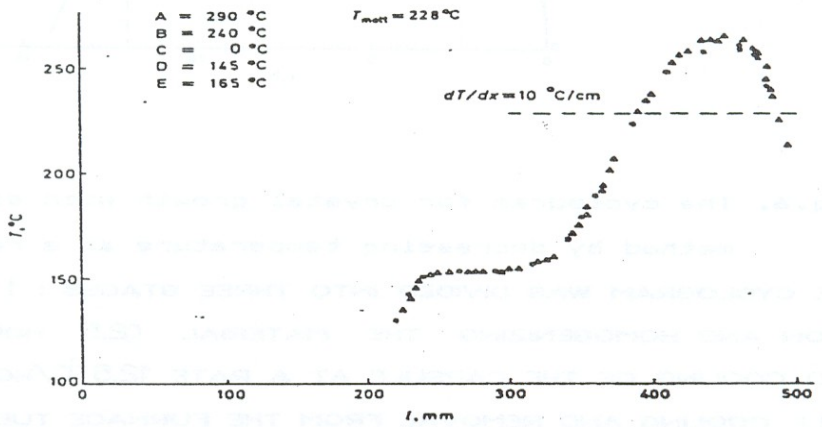


Fig.5. The temperature gradient in CSK-1 equipment formed by five heater sections (A, B, C, D, E)

TO INCREASE THE RALIABILITY AND INFORMATION CAPACITY OF THE EXPERIMENT, TWO CYCLOGRAMS WERE PREPARED. ONE IS FOR THE CRYSTAL GROWTH WITH DIRECT COOLING METHOD BY SUCCESSIVELY DECREASING HEATER TEMPERATURES AT A RATE 12.5 °C/HOUR IN A STATICAL POSITION OF CAPSULE MOUNTED INTO CSK-1 APPARATUS. THIS CYCLOGRAM IS PRESENTED IN FIG.6.

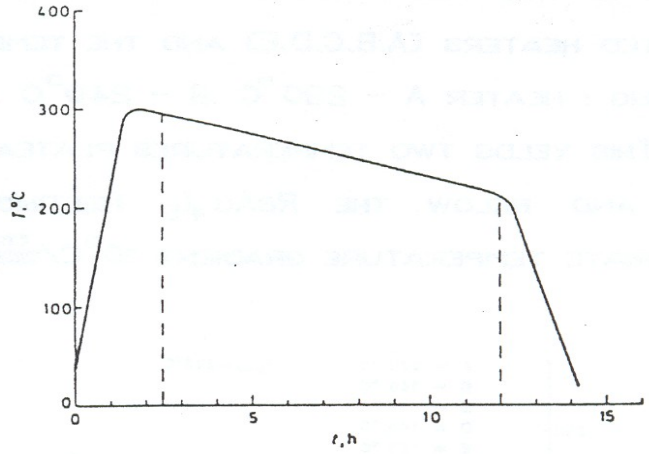


Fig.6. The cyclogram for crystal growth with direct cooling method by decreasing temperature at a rate 12.5°C/h

THE CYCLOGRAM WAS DIVIDED INTO THREE STAGES : 1 - SWITCHING FURNACE ON AND HOMOGENIZING THE MATERIAL (2.5 HOURS) ; 2 - CONTROLED COOLING OF THE CAPSULE AT A RATE 12.5 °C/HOUR (9.5 HOURS) 3 - SAMPLE COOLING AND REMOVAL FROM THE FURNACE TUBE. THIS METHOD LEADS TO A SMOOTH SHIFT OF THE FRONT OF CRYSTALLIZATION.

THE SECOND METHOD USED FOR CRYSTALLIZATION IS BY CAPSULE MOVING THROUGH THE GRADIENT ZONE AT A RATE 5 MM / HOUR. THE CYCLOGRAM IS SHOWN IN FIG.7 WHERE WERE DIVIDED ALSO THREE STAGES : 1 - SWITCHING FURNACE ON AND HOMOGENIZING THE MATERIAL ; 2 -SAMPLE MOVING AT 40 MM VIA THE GRADIENT ZONE (9.5 HOURS) ; 3 - SAMPLE COOLING AND REMOVAL FROM THE FURNACE TUBE.

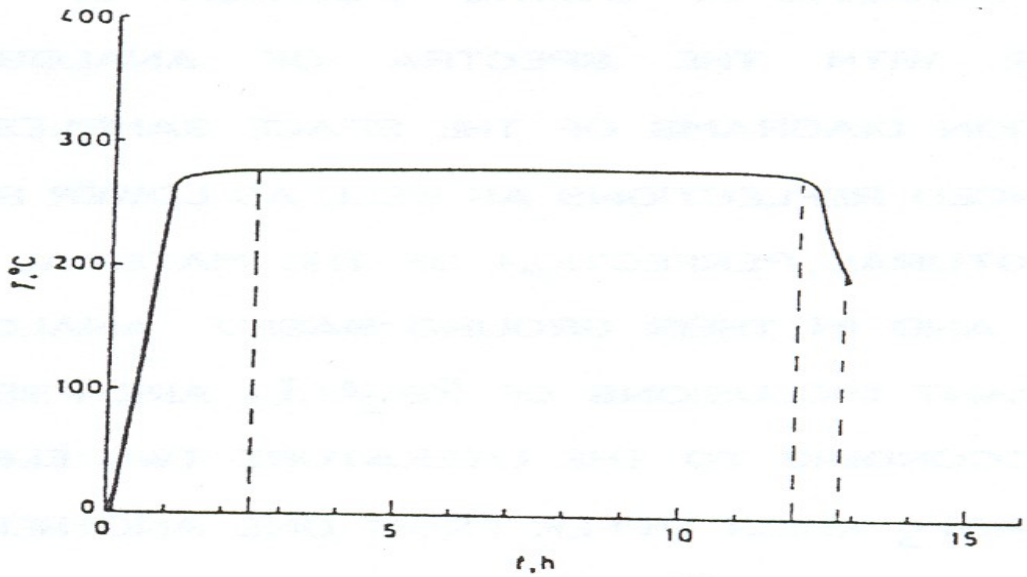
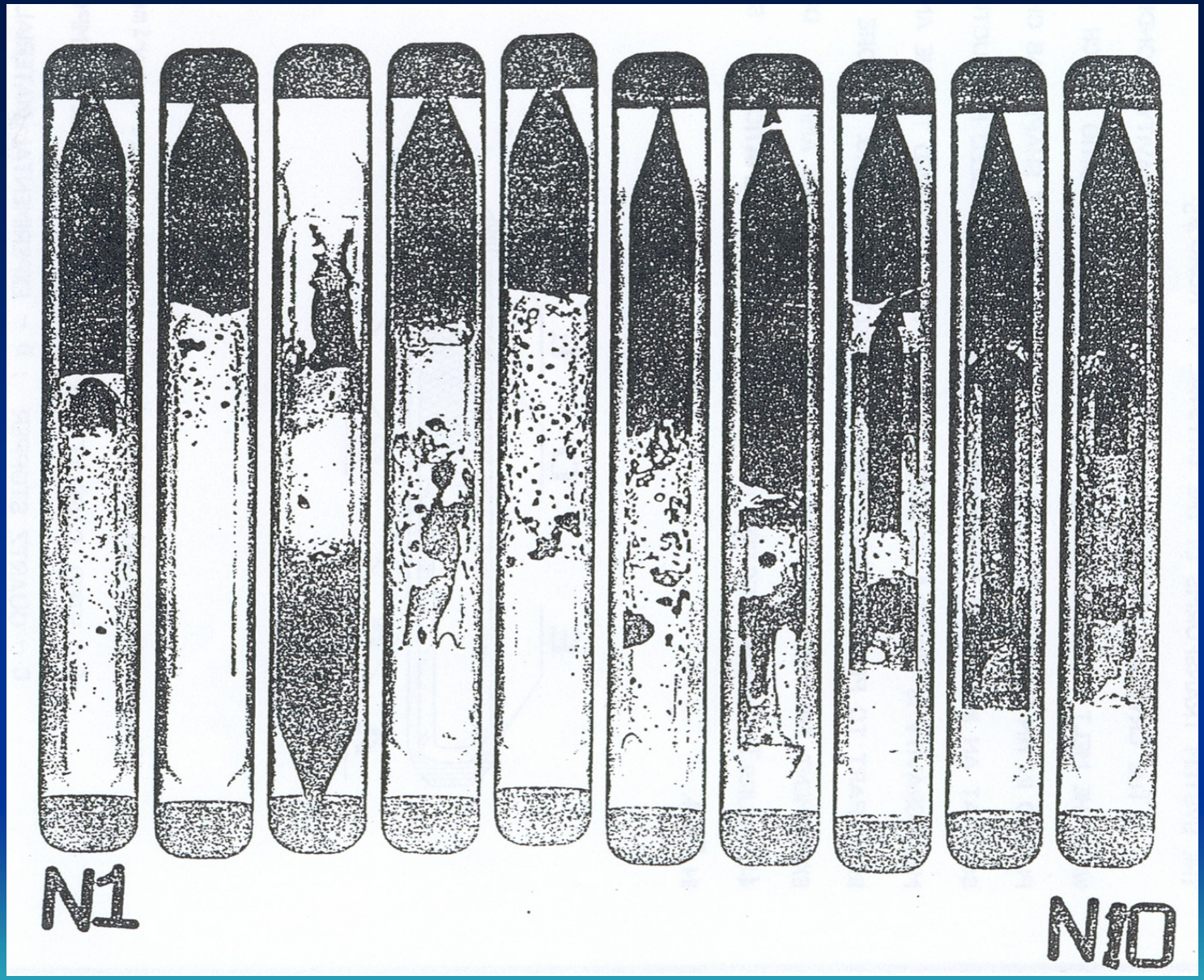


Fig.7. The cyclogram for crystal growth by capsule moving through the gradient zone at a rate 5 mm/h


N1
N10

X-ray analysis of $RbAg_4J_5$ - crystals

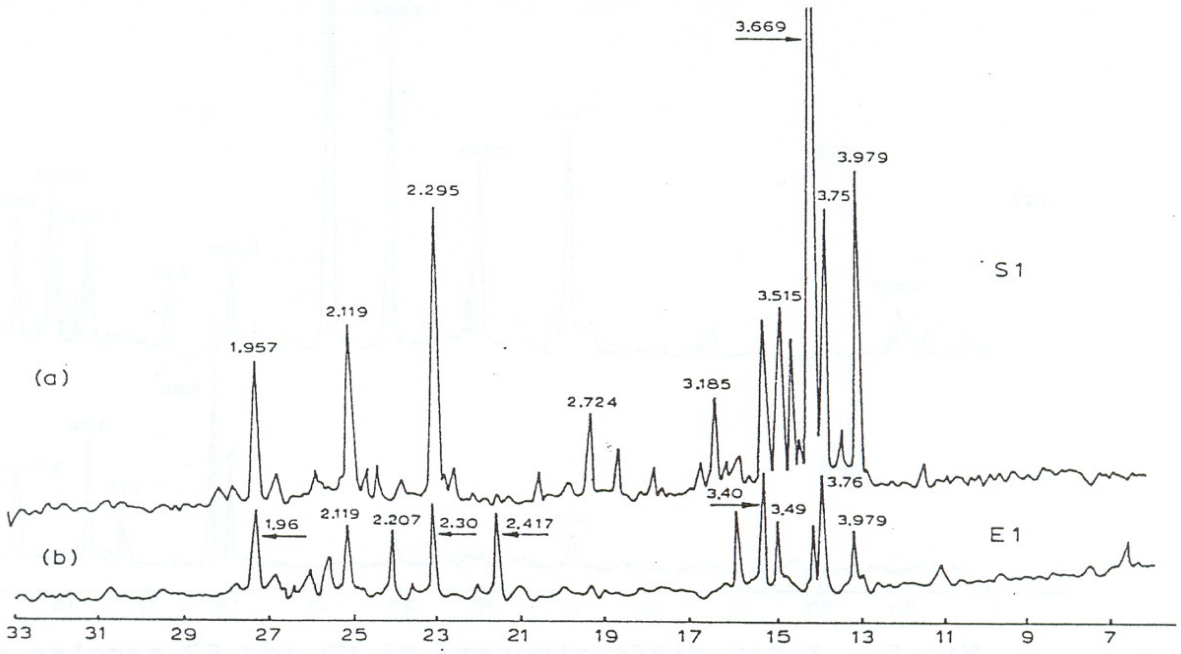


Fig.8 X-ray diffractograms of S1 and E1 crystals obtained by moving of front of crystallization

INTENSIVE PEAK AT 3.669Å IS ONE OF THE RbI. THE SET OF AgI PEAKS AT 3.75Å , 3.5Å , 2.72Å , 2.29Å , 2.119Å , 1.95Å ALSO INDICATE THE PRESENCE OF AgI PHASE IN THE SPECTRUM OF S1.IT IS POSSIBLE TO ASSUME THAT IN THIS CONDITIONS FRONT PHASE SEGREGATION APPEARS AND RbI AND AgI PHASES ARE INCORPORATED IN THIS INGOT.

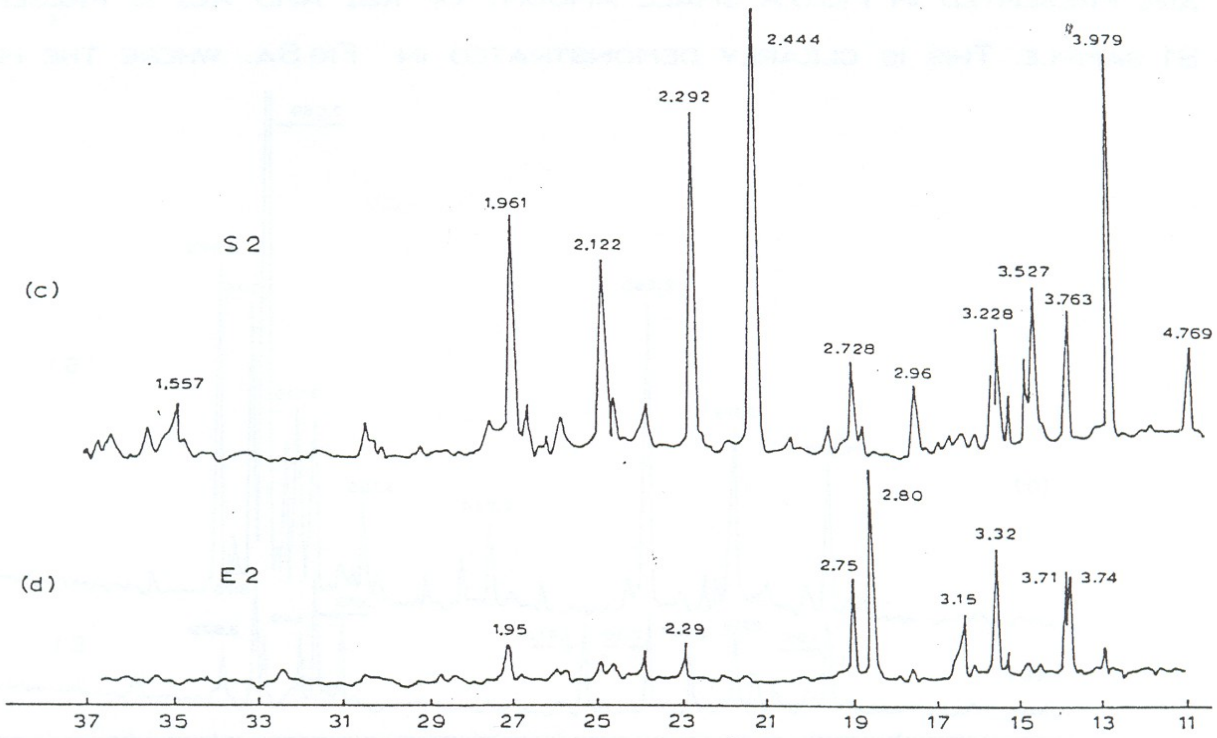


Fig.9. X-ray diffractograms of S2 and E2 samples obtained by cooling method in static position of capsule

THE S2 SAMPLE IS ALSO MULTIPHASE BUT OF DIFFERENT PHASE DISTRIBUTION. THE MOST INTENSIVE PEAK AT 2.444A IS CHARACTERISTIC FOR BOTH $RbAg_4I_5$ AND Rb_2AgI_3: THE INTENSITIVE LINE AT 3.97A IS PRESENT IN BOTH $RbAg_4I_5$ AND AgI. SO,IN THIS TECHNOLOGICAL REGIME THE $RbAg_4I_5$, Rb_2AgI_3 AND AgI PHASES ARE OBTAINED.

Scaning electron microscope analysis

INVESTIGATION OF THE SURFACE OF THE SAMPLES BY SCANNING ELECTRON MICROSCOPE SHOWS ALSO DIFFERENCES IN THE SURFACE MORPHOLOGY OF THE EARTH AND SPACE SAMPLES.ONE OF THE PICTURES OF THE SLICES FROM E2 AND S2 INGOTS IS SHOWN IN FIG.10. IN THE LEFT PART THE SURFACE STRUCTURE OF E2-SAMPLE IS PRESENTED AND IN THE RIGHT PART - THAT OF S2.IT IS OBVIOUS THAT THE SURFACE OF SPACE

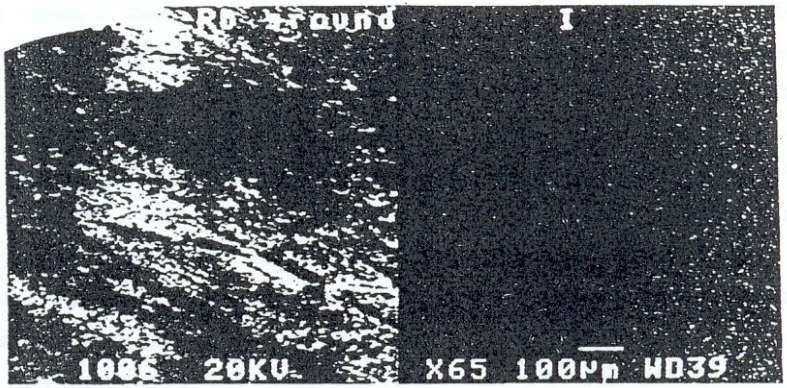


Fig.10. Surface structure of the earth (E2) - [left] and space (S2) - [right] samples of $RbAg_4I_5$

CRYSTAL IS MORE HOMOGENEOUS.ALSO THE MICROPROBE WAS USED TO ANALYZE THE MATERIAL COMPOSITION IN VARIOUS PARTS OF SAMPLE SLICES.THE STUDIES EVIDENCED SOME DIFFERENCES IN THE CONCENTRATION OF ELEMENTS.WHICH IS IN AGREEMENT WITH THE PRESENCE OF TWO COMPOUNDS IN THE MATERIAL.SPACE SAMPLES OBTAINED BY DIRECTIONAL SOLIDIFICATION APPEARED TO BE MOST HOMOGENEOUS ACCORDING TO THE MICROPROBE ANALYSIS.THE CONTENTS OF Rb , Ag AND I ARE 10.765%.

Photoluminescence spectra

THE PHOTOLUMINESCENCE SPECTRA OF THE SAME SAMPLES ARE TAKEN AT 77K WITH ULTRAVIOLET EXCITATION FROM MERCURY LAMP DRS-500. THEY ARE RESOLVED BY A GRATING MONOCHROMATOR MDR-23 AND REGISTERED BY LOCK-IN AMPLIFIER. FOR ALL SAMPLES WE OBSERVED TWO CHARACTERISTIC PEAKS : λ_{max1} = 2.75 eV AND λ_{max2} = 2.92 eV BESIDES THE BAND EDGE RECOMBINATION AROUND 3.4 eV. THE SPECTRA OF THE SAMPLES (S1 , E1) AND (S2 , E2) ARE SHOWN IN FIG.11. THE DOUBLE PEAK STRUCTURE IS KNOWN TO BE CONNECTED WITH THE LUMINESCENCE OF AgI AND RbI INCORPORATIONS. THE STRONG DIFFERENCE IN THE INTENSITY OF THE PEAK CENTERED AT 2.92 eV IN BOTH SAMPLES WE ATTRIBUTE TO THE DIVERSE PHASE DISTRIBUTION IN THE TWO SAMPLES WHICH WE ALREADY DISCUSSED.

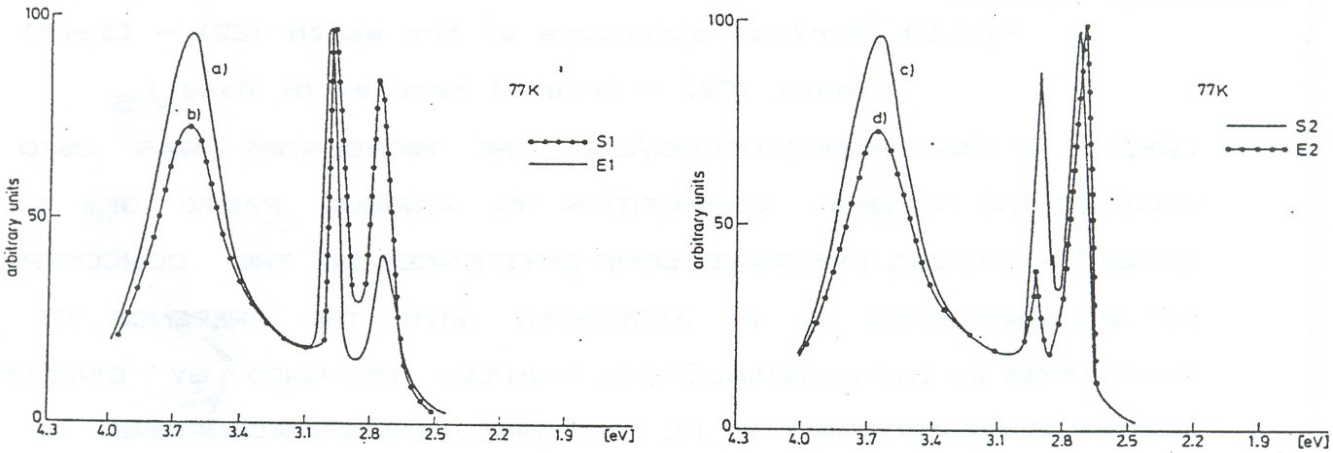


Fig.11. Photoluminescence spectra of space and earth samples

Raman spectra of space samples

THE NON-ELASTIC RAMAN SCATTERING BY OPTICAL PHONONS HAS A POSSIBILITY FOR DETERMINATION OF ENERGY, IMPULSE, LIFE TIME AND SYMMETRY OF ELEMENTARY EXCITATION. THE ENERGY ($\hbar\omega$) IS OBTAINED BY DISCREPANCY BETWEEN THE FREQUENCIES OF INCIDENT AND SCATTERING LIGHT ($\omega = \omega_i - \omega_s$). THE IMPULSE ($\hbar k$) IS DETERMINED BY DISCREPANCY BETWEEN WAVE VECTORS ($k = k_i - k_s$). THE LIFE TIME τ IS THE RECIPROCAL MAGNITUDE OF SPECTRAL WIDTH Γ. THE SYMMETRY OF ELEMENTARY EXCITATIONS DETERMINES BY POLARIZATION EFFECTS. THE TYPICAL RAMAN SPECTRUM FOR α-AgI IS VERY LARGE AND CONTINUES TO 240 CM^{-1} WITHOUT SHARP PEAKS WHICH IS USUAL FOR THE DISORDERED STRUCTURE OF SUPERIONIC α - PHASES. THE INTENSITY SCATTERING DECREASES VERY FAST WITH THE MOVE OFF FROM THE ZERO LASER FREQUENCY. AN ANALOGICAL SPECTRUM FOR $RbAg_4I_5$ WAS OBSERVED BY GALLAGHER WHERE IS REGISTERED ONE LARGE PEAK AT 107 CM^{-1} ONLY. IT IS CONNECTED WITH IODIDE TETRAHEDRAL EXTENSION. THE RAMAN SPECTRA OF OTHER COMPOUND Rb_2AgI_3 WHICH IS NOT SUPERIONIC MATERIAL CONTAIN A SIMILAR PEAK IN THE REGION 110 CM^{-1} , BUT SLIGHT PEAKS UNDER 80 CM^{-1} ARE REGISTERED.

THE LARGE SPECTRA OF AgI AND $RbAg_4I_5$ ARE CONNECTED WITH DIFFERENT FORCES BETWEEN IONS AND WITH HOPPING MOVEMENT OF SILVER

THE RAMAN SPECTRUM OF $RbAg_4I_5$ SAMPLES OBTAINED IN MICROGRAVITY CONDITIONS IS SHOWN IN FIG.12.

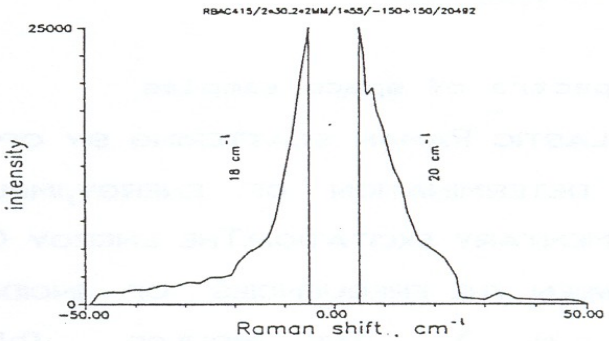


Fig.12. Raman spectra of space $RbAg_4I_5$ crystals

IT DILATES TO 40 cm^{-1} AND THE PEAK AT THE REGION 20 cm^{-1} IS OBSERVED.THE RELATIVELY NARROW SPECTRUM SHOWS THAT THE CRYSTAL STRUCTURE OF THE SPACE SAMPLES IS BETTER THAT THE STRUCTURE OF THE EARTH ONES.THE LOW FREQUENCY PEAK AT 20 cm^{-1} IS CONNECTED WITH DIFFUSION OF SILVER CATIONS.IT WAS REGISTERED UP TO NOW IN α-AgI CRYSTALS WITH GOOD STRUCTURES ONLY.THE ABSENCE OF THIS PEAK IN THE RAMAN SPECTRA OF $RbAg_4I_5$ - EARTH CRYSTALS IS DUE TO NON-IDEAL STRUCTURE.THEREFORE,THE PRESENCE OF 20 cm^{-1}-PEAK IN RAMAN SPECTRA OF SPACE SAMPLES ONLY IS GUARANTEE FOR THE CRYSTAL QUALITY.ONE

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