Chapter - 5

Summary, Conclusions and Scope for the Future
5. SUMMARY, CONCLUSIONS AND SCOPE FOR THE FUTURE

This Chapter provides a summary of the research work carried out together with the conclusions derived in the present study. Scope for the future is also provided here.

5.1. Summary and Conclusions

The solid solutions of alkali halides indeed constitute a very interesting system for optical information storage devices. The study of physical properties of alkali halides has been a subject of interest in the recent past. Crystals are grown artificially every day and now we are more concerned to discover new materials for the purpose of academic and industrial uses. There is an increasing demand for crystals of complex composition comprising of mixed and doped materials. So scientists’ interests have turned from pure crystals to mixed crystals. Just like the alkali halides their mixed crystals are also equally important. Alkali halide mixed crystals are the completely disordered substitutional type.

Aiming at discovering new materials, in the present research work, an attempt was made to grow polycrystals of: Na\(_x\)K\(_{1-x}\)Br mixed crystals (x = 0.2, 0.4, 0.5, 0.6 and 0.8); ZnS added NaCl, NaBr, KBr, (NaCl)\(_{0.5}\)(KBr)\(_{0.5}\) and Na\(_{0.5}\)K\(_{0.5}\)Br crystals; mixed crystals from miscible NaBr and KCl; end members, viz. NaCl, NaBr, KCl and KBr; etc and characterize the grown crystals.
Binary and ternary (obtained as outcome) solid solutions of NaCl, NaBr, KCl and KBr were grown by the (cooled) melt method. A total of twenty (mixed and end member) crystals were grown by the above method and under identical conditions. The end member crystals were grown for comparison purposes.

Densities of all the grown solid solutions were determined by using the floatation method. Refractive indices of the crystals were determined by using the Gladstone’s rule. Compositions of the grown crystals were estimated by using the density and refractive index values and assuming the additive rule satisfying for them. AAS data were collected for some systems to confirm the estimated composition (metal atom contents).

An automated X-ray diffractometer was used to collect the X-ray diffraction data from powder samples of crystals. The reflections were indexed using the conventional procedures. Lattice parameters were determined using the available methods.

X-ray powder diffraction intensity (integrated) data were used to determine the thermal parameters like Debye-Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency. Mean Debye-Waller factors were determined by the Wilson plot method and other thermal parameters were determined from the Debye-Waller factor using the Debye-Waller theory. Compressibility and mean sound velocity were determined using the Debye temperature value.

DC electrical conductivities were measured for all the twenty grown crystals at various temperatures ranging from 35 to 150°C by using the conventional two-probe method. Activation energies and mean jump frequencies were also determined.
Capacitance and dielectric loss tangent (tand) measurements were carried out for all the twenty grown crystals at various temperatures ranging from 35 to 150°C using an LCR meter with a fixed frequency of 1 kHz. Dielectric constants, AC electrical conductivities and activation energies were determined from the measured capacitance and tand values.

UV-Vis and FTIR spectra were recorded for all the twenty grown crystals and UV-Vis and IR transmittances noted.

The grown mixed crystals are found to be more hard and less transparent when compared to the end member crystals. Density and refractive index values, lattice and thermal parameters and dielectric constants observed in the present study for the end member crystals compare well with those reported in the literature. The metal atom contents (in the composition) estimated using density and refractive index values compare well with those obtained through AAS data.

The thermal parameters are found to vary non-linearly with composition. Variation in these parameters may be attributed to the variation in vibrational entropy due to mixing. The conductivity was found to increase with the increase in temperature but vary non-linearly with composition. However the conductivity is found to be more for the mixed crystals than the end member crystals. The observed non-linear variation of DC conductivity, activation energy and mean jump frequency has been explained as due to the enhanced diffusion of charge carriers along dislocations and grain boundaries which are more in mixed crystals.
The dielectric constants are found to increase with the temperature for all the crystals. However, the bulk composition has complicated influences on the dielectric constant, \( \sigma_{dc} \) and \( E_{ac} \) values. This non-linear variation has been attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries. The influence of anharmonicity of lattice vibration has been attributed to this non-linear variation. In addition, the multiphased binary mixed crystals and ZnS added crystals are found to have large dielectric constants and are expected to be more useful than the end member crystals.

The recorded UV-Vis spectra show the absorbing power of the system which does not vary with the composition in any systematic manner. The FTIR spectra show the transparent nature in the defined frequencies assigned for the various systems considered in the present study.

All the mixed crystals (binary and ternary) grown are of multiphased and are expected to be more useful than the end member crystals though their internal structures contain multiple phases. Also, the present study indicates the possibility of preparing multiphased binary, ternary etc mixed alkali halide crystals using the miscible NaBr and KCl as the starting materials.

The present study has indicated that the ZnS addition significantly changes the density and refractive index values, lattice and thermal parameters, electrical conductivity and dielectric constant values, etc in both the pure and mixed alkali halide crystals grown. Although the depth profile study has not been carried out, the light greenish colouration (especially in the case of ZnS added NaCl) indicates that ZnS addition creates different layers in the crystal with increase of ZnS content from top to bottom.
In effect, the present study indicates that the multiphased mixed crystals and ZnS added crystals grown are having more hardness and high dielectric constants and are expected to be more useful than the end member crystals.

5.2. Scope for the Future

Crystal growth and characterization is an important field of materials science which has got scientific as well as technological importance. Studies on crystalline materials normally involve the following:

(i) Nucleation and growth of crystals;
(ii) Structural and physical characterization;
(iii) Growth of large crystals;
and (iv) Fabrication of devices with the grown crystals; etc.

Scientific research on crystalline materials is normally constituted by the (above mentioned) first two types of studies while the technological research is constituted by the remaining two types. The present research work (reported in this thesis) is of scientific nature and not technological.

Alkali halide crystals are widely used as laser window materials, neutron monochromators, infrared prisms, infrared transmitters, etc. The solid solutions of alkali halides constitute a very interesting system for optical information storage. Studies on the growth of single crystals of poly component system is a complicated process. But the use of pure alkali halides are limited by the mechanical systems and hence there exist the need to strengthen them. The mixed and impurity added (doped) crystals of alkali halides are found to be harder than the end members and so they are more useful in these applications.
In view of the overall importance of the alkali halides there has been continuing activity in all aspects of alkali halides. As a result, a wide body of literature is also available for these materials.

In the present work, some investigations have been carried out on the growth and characterization of: (i) multiphased Na<sub>x</sub>K<sub>1-x</sub>Br crystals for x = 0.2, 0.4, 0.5, 0.6 and 0.8; (ii) ZnS added NaCl, NaBr, KCl Na<sub>0.5</sub>K<sub>0.5</sub>Br and (NaCl)<sub>0.5</sub>(KBr)<sub>0.5</sub> crystals; (iii) multiphased mixed crystals from miscible NaBr and KCl; (iv) the end member crystals, viz. NaCl, NaBr, KCl and KBr; etc. As our aim was to grow crystals needed for characterization only, growth of large crystals required for device fabrication were not carried out. As the grown solid solutions are found to be harder than pure crystals, its application in device fabrication is expected to bring good results in the future.

In the present investigation on the different binary solid solutions, x is varied as 0.2, 0.4, 0.5, 0.6 and 0.8. Further it can be extended for other values of x, namely, 0.1, 0.3, 0.7 and 0.9, so that it may help to obtain relationship between composition and other properties in a better manner. For the ZnS added system, the percentage of ZnS can be varied which may be expected to yield fruitful results.

Depth profile study of these crystals are necessary for a full understanding of these materials. Other II – VI compounds may also be considered. X-ray diffraction studies can be extended to find out atomic positions.

Conductivity measurements are limited to various temperatures ranging from 35-150°C. Conductivities in this temperature region of mixed crystals are found to be greater
than that of end member crystals. More useful results can be derived, if the study is extended to lower and higher temperatures.

Dielectric studies may be extended to lower and higher temperatures and at different frequencies.

Etching, microhardness and thermoluminescence studies on these solid solutions may yield fruitful results. So, still more investigations are needed to be carried out for a better understanding of the materials and thereby to find out good applications.

Growth of single crystals of the systems considered in the present study using a Czochralski puller and characterizing the same may also yield a good understanding of these materials for use in various devices.