GENERAL CONCLUSION

Mixed rare earth oxalate crystals of PSO, NSO, and NPO were grown using the gel technique. A detailed study of the characteristics of the crystals was also undertaken.

The gel method accepted as the unique technique for the growth of oxalate class of materials was employed in the present study. The optimum conditions for the growth of high quality single crystals were determined by adjusting the various growth conditions and the results are given below.

Optimum conditions for the growth of mixed rare earth oxalate crystals.

- Gel density: 1.03 gm/cc
- Gel age: 24 hrs
- pH of the gel: 6
- Inner reactant: 1 M oxalic acid
- Outer reactant: 1 M solutions of rare earth

Acid content in the feed solution: Conc. HNO₃, 25% by volume of the feed solution.

Growth period: 4 weeks. The morphology of the crystal was found to vary with the growth environment.

The effect of various gel parameters such as the density, pH and age of the gel, concentration of the reactants, etc. were altered in order to minimize the nucleation density. The variation of the nucleation density with all these parameters have been studied extensively. The experiments revealed that the addition of a
certain amount of acid into the feed solution is the most effective technique to control nucleation. The advantage of this technique is that it considerably reduces the nucleation density without affecting the quality of the crystal.

The surface features of the grown crystals were apparently the same. All the three types of crystals showed regular patterns of growth layers on the (100) plane. The identical habit of the surface of the crystals is a clear evidence for the congenital likeness of PSO, NSO and NPO crystals, which reflects well during the structural investigations. This was further confirmed during the dislocation studies. An exact identity was found in the nature of etch pits during the etching of the (100) and (110) faces of all the crystals. The existence of dislocations is clearly evident from the one to one correspondence between the etch pits on the matched cleaved faces.

The X-ray powder diffraction analysis of the grown crystals of NSO, NPO and PSO revealed their identical Bragg’s diffraction planes. Calculated values of the lattice parameters matched well with that of NO, PO and SO. This suggests that the mixed rare earth oxalate also crystallize in the monoclinic system with space group $P2_1/n$ as that of the single rare earth oxalates. The proposed chemical formula for these crystals are $\text{NdPr(C}_2\text{O}_4)_3\cdot10\text{H}_2\text{O}$, $\text{NdSm(C}_2\text{O}_4)_3\cdot10\text{H}_2\text{O}$ and $\text{PrSm(C}_2\text{O}_4)_3\cdot10\text{H}_2\text{O}$. The presence of water of hydration and the oxalate group are established by the IR absorption studies and the proposed chemical formula is also well established by the thermal analysis of the crystals. The various steps during the thermal decomposition of this class of mixed oxalate crystals is in accordance with

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\begin{align*}
\text{RR}'\text{(C}_2\text{O}_4)_3\cdot10\text{H}_2\text{O} & \rightarrow \text{RR}'\text{(C}_2\text{O}_4)_3\cdot3\text{H}_2\text{O} \\
& \rightarrow \text{RR}'\text{(C}_2\text{O}_4)_3 \\
& \rightarrow \text{RR}'\text{O}_2\text{CO}_3 \\
& \rightarrow \text{RR}'\text{O}_3
\end{align*}
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The existence of a dioxycarbonate formed as an intermediate decomposition product is clear from the thermal analysis data. The final product is mixed rare earth oxalate. The liberation of water molecules from the crystals in steps of 7 and 3 is in accordance with the proposed crystal structure, in which three are attached to the lattice and the other seven molecules are disordered in the intervening space of the lattice. The attached water molecules liberate from the crystal very slowly. The XPS and EDAX studies were carried out to identify various rare earths present in the grown crystals both qualitatively and quantitatively. It is observed that a series of stoichiometric compounds of mixed rare earth oxalates can be prepared by the simple adjustment of the proportions of the rare earths in the feed solutions. The VSM technique has been utilized to determine the magnetic behavior of the grown samples.

The various spectroscopic parameters are evaluated for NPO crystals based on the Judd-Ofelt theory. Since NPO sample contains Nd$^{3+}$ and Pr$^{3+}$ as the luminescence centers, the calculations are done separately for these ions. The branching ratio and emission cross-section are found to be maximum for the 3P$_o$ level of Pr$^{3+}$. The emission from this level will give the maximum optical gain.

Mixed rare earth oxalate crystals have a lot of potentialities in technical field due to their interesting magnetic and luminescent properties. Further studies can be attempted to grow more perfect and bigger crystals useful for industrial applications.