GROWTH AND CHARACTERIZATION OF COLORED AND MONODOMAIN CRYSTALS OF KH₂PO₄-TYPE OF FERROELECTRICS AND ANTIFERROELECTRICS

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Abstract Techniques are described for growing colored and single crystals of KH₂PO₄-type ferroelectric and antiferroelectrics. The color centers are identified by EPR and optical spectroscopy.

INTRODUCTION

KH₂PO₄-type of ferroelectrics and antiferroelectrics are widely used as non-linear dielectric devices in laser technology, for example as elements for laser frequency multiplication and fast optical switches.¹ It is also known that the interaction of the laser light with these crystals will depend on the pattern of the ferroelectric or antiferroelectric domain pattern normally present in their ferroelectric or antiferroelectric phases.¹ In order to obtain higher light output and, in particular, selectivity for certain desired laser frequencies, it was thought worthwhile to investigate the growth of single crystals with specific absorption bands and for which the ferroelectric or antiferroelectric domain pattern could be significantly controlled. In this presentation we summarize our results of such investigations. We report that it is possible to grow optical quality crystals of the KH₂PO₄-type ferroelectrics and NH₄H₂PO₄-type antiferroelectrics with color ranging from blue to orange. The identity of the color centers has been made by electron paramagnetic resonance (EPR) and optical absorption techniques, and these centers have been found to be useful probes for investigating the roles of specific ionic fragments in the
mechanism(s) of phase transitions in the host compounds. It is also noted that while the domain pattern of the ferroelectric samples can be altered by means of externally applied electric field, that of the antiferroelectric samples can be affected by crystal growth conditions and temperature cycling through the phase transitions.

GROWTH AND OPTICAL ABSORPTION OF COLORED CRYSTALS

Optical quality colored crystals of all KH$_2$PO$_4$-type compounds can be grown at room temperature (~25°C) by natural evaporation of a partially saturated solution of a host compound in which about 0.1-5% (by weight) of a suitable dopant had been dissolved. Since all pure (undoped) crystals of the KH$_2$PO$_4$-family are colorless, the color of the doped crystals will be characteristic of the dopant, modified somewhat by the lattice effects of the host. For example, yellowish crystals of KH$_2$PO$_4$ can be grown from a partially saturated solution of KH$_2$PO$_4$ containing a ~1% by weight of K$_2$CrO$_4$. While quantitative measurements were not made, it was noted that up to about 5% limit, the visual intensity of the coloration of a doped crystal was proportional to the amount of the dopant dissolved into the crystal growth solution.

In several cases the doped crystals were initially colorless but acquired intense, stable coloration on irradiation with X-rays or γ-rays. Here the coloration was a result of the conversion of the doped ions into color centers, and the coloration intensity could be controlled both by varying the amount of the dopant and the irradiation dose. Usually a few hours of γ-irradiation from a $^{60}$Co source was sufficient to obtain an intense color. In most cases these color centers were identified by EPR spectroscopy, as discussed elsewhere, unless specified otherwise.

Table 1 summarizes the optical properties of all KH$_2$PO$_4$-type crystals investigated so far.
TABLE 1  Optical properties of the doped and/or irradiated crystals of the KH₂PO₄-family.

<table>
<thead>
<tr>
<th>Host</th>
<th>Color</th>
<th>Dopant</th>
<th>Color Center</th>
<th>λ_max (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>Yellow</td>
<td>K₂CrO₄</td>
<td>CrO₄²⁻</td>
<td>2700, 3600</td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>Brown</td>
<td>HgCl₂⁺</td>
<td>Hg⁺</td>
<td>3050</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>Green</td>
<td>K₂CrO₄⁺</td>
<td>CrO₄³⁻</td>
<td>5000, 5500</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>Blue</td>
<td>Na₂WO₄⁺</td>
<td>WO₄³⁻</td>
<td>6200</td>
</tr>
</tbody>
</table>

a KH₂PO₄, KH₂AsO₄, KD₂AsO₄, NH₄H₂AsO₄, ND₄D₂AsO₄, NH₄H₂PO₄ and ND₄D₂PO₄ exhibit a similar coloration.
b KH₂PO₄, KD₂PO₄ and ND₄D₂PO₄ exhibit similar coloration and EPR signals.
c NH₄H₂PO₄ exhibits an essentially similar color and EPR signal.

IDENTIFICATION OF COLOR CENTERS

CrO₄²⁻

CrO₄²⁻ was identified by comparison with its optical absorption spectra reported earlier.³,⁴ There are two main absorption bands around 3600 and 2700 Å. These bands can be satisfactorily explained on the basis of the molecular orbital scheme proposed by Viste and Gray.⁵ Both bands are assigned to a ¹A₁ → ¹T₂ transition which is orbitally allowed in T₄d symmetry. The 3600 Å band shows a considerable vibronic structure at 80 K, with an average spacing of about 760 cm⁻¹. This might be assigned to the totally symmetric stretching mode of CrO₄²⁻ ion in the excited state.⁶

As noted in Table 1, CrO₄²⁻ can be stabilized in all of the
KH$_2$PO$_4$-type ferroelectrics and antiferroelectrics.

Hg$^+$ Ion

Hg$^+$ (6s$^1$) ion shows an absorption band at about 3050 Å, as reported by Eachus and Herring. This center is identified mainly by its EPR spectra where the hyperfine structure is characterized by its much larger value (~35 GHz) as compared to the Zeeman term at X-band (9 GHz).

CrO$_4$$^{3-}$

This center, formed on γ-irradiation of CrO$_4$$^{2-}$ doped compounds, exhibits absorption bands around 5000, 5500 and 6000 Å, but its identity is made certain only through EPR spectroscopy. This center can also be stabilized in all of the KH$_2$PO$_4$ compounds.

WO$_4$$^{2-}$

KH$_2$PO$_4$ and NH$_4$H$_2$PO$_4$ crystals, when doped with ~1% WO$_4$$^{2-}$ and γ-irradiated at room temperature exhibit intense blue coloration and concomitant EPR signals with g-values in the range expected for d$^1$ electron in a d$_{x^2-y^2}$ ground state. Some of the EPR spectra exhibit axial symmetry about the crystal c-axis, as would be expected if the WO$_4$$^{2-}$ ions substituted PO$_4$$^{3-}$ ions. Further EPR studies are in progress to identify the color center responsible for the blue coloration in these crystals.

MONODOMAIN CRYSTALS

As is well known, all of the ferroelectric crystals can be made into single domain by the application of external, DC electric fields of the order of 10 kV/cm along the crystalline c-axis. We have found that the doped crystals can also be poled by the same method.

Of course the antiferroelectric crystals cannot be made into a single domain by using electric fields. We found, however, that for NH$_4$H$_2$AsO$_4$, ND$_4$H$_2$AsO$_4$, NH$_4$H$_2$PO$_4$ and ND$_4$D$_2$PO$_4$, a rapid
Crystal growth from a nearly supersaturated solution frequently resulted in predominantly monodomain samples. The monodomain character was confirmed via EPR measurements showed that these samples exhibited only half the number of EPR lines compared to the crystals normally grown. Furthermore, it was found that the monodomain character could be enhanced via temperature cycling of the crystals through their phase transitions. Some crystals (particularly NH$_4$H$_2$PO$_4$) cracked during this temperature cycling but several remain single and exhibited a more pronounced monodomain character. We believe that this observation would be helpful for enhancing spectroscopic resolution from the antiferroelectric crystals.

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**REFERENCES**