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GROWTH AND CHARACTERIZATION OF COLORED AND MONODOMAIN CRYSTALS OF KH_2PO_4-TYPE OF FERROELECTRICS AND ANTIFERROELECTRICS

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Abstract Techniques are described for growing colored and single crystals of KH_2PO_4-type ferroelectric and antiferroelectrics. The color centers are identified by EPR and optical spectroscopy.

INTRODUCTION

KH_2PO_4-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 KH_2PO_4-type ferroelectrics and $NH_4H_2PO_4$-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.[2] 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_2PO_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_2PO_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_2PO_4 can be grown from a partially saturated solution of KH_2PO_4 containing a ~1% by weight of K_2CrO_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[2], unless specified otherwise.

Table 1 summarizes the optical properties of all KH_2PO_4-type crystals investigated so far.

TABLE 1 Optical properties of the doped and/or irradiated crystals of the KH_2PO_4-family.

Host	Color	Dopant	Color Center	λ_{max} (Å)
KH_2PO_4[a]	Yellow	K_2CrO_4	CrO_4^{2-}	2700, 3600 5000–7000
$NH_4H_2PO_4$[b]	Brown	$HgCl_2$ + γ-irradiation	Hg^+	3050
KH_2PO_4[a]	Green	K_2CrO_4 + γ-irradiation	CrO_4^{3-}	5000, 5500 6000
KH_2PO_4[c]	Blue	Na_2WO_4 + γ-irradiation	WO_4^{3-}	6200

[a] KD_2PO_4, KH_2AsO_4, KD_2AsO_4, $NH_4H_2AsO_4$, $ND_4D_2AsO_4$, $NH_4H_2PO_4$ and $ND_4D_2PO_4$ exhibit a similar coloration.

[b] KH_2PO_4, KD_2PO_4 and $ND_4D_2PO_4$ exhibit similar coloration and EPR signals.

[c] $NH_4H_2PO_4$ exhibits an essentially similar color and EPR signal.

IDENTIFICATION OF COLOR CENTERS

CrO_4^{2-}

CrO_4^{2-} 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 $^1A_1 \rightarrow {}^1T_2$ transition which is orbitally allowed in T_d 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 CrO_4^{2-} ion in the excited state.[6]

As noted in Table 1, CrO_4^{2-} can be stabilized in all of the

KH_2PO_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.[7] This center is identified mainly by its EPR spectra[7,8] 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,[4] but its identity is made certain only through EPR spectroscopy.[2] This center can also be stabilized in all of the KH_2PO_4 compounds.

WO_4^{3-}

KH_2PO_4 and $NH_4H_2PO_4$ crystals, when doped with ~1% WO_4^{2-} and γ-irradiated at room temperature exhibit intense blue coloration and concommitant 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[1,2], 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[2,9] 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 $NH_4H_2AsO_4$, $ND_4H_2AsO_4$, $NH_4H_2PO_4$ and $ND_4D_2PO_4$, a rapid crystal growth from a nearly supersaturated solution frequently resulted in predominatly 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[10] via temperature cycling of the crystals through their phase transitions. Some crystals (particularly $NH_4H_2PO_4$) 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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